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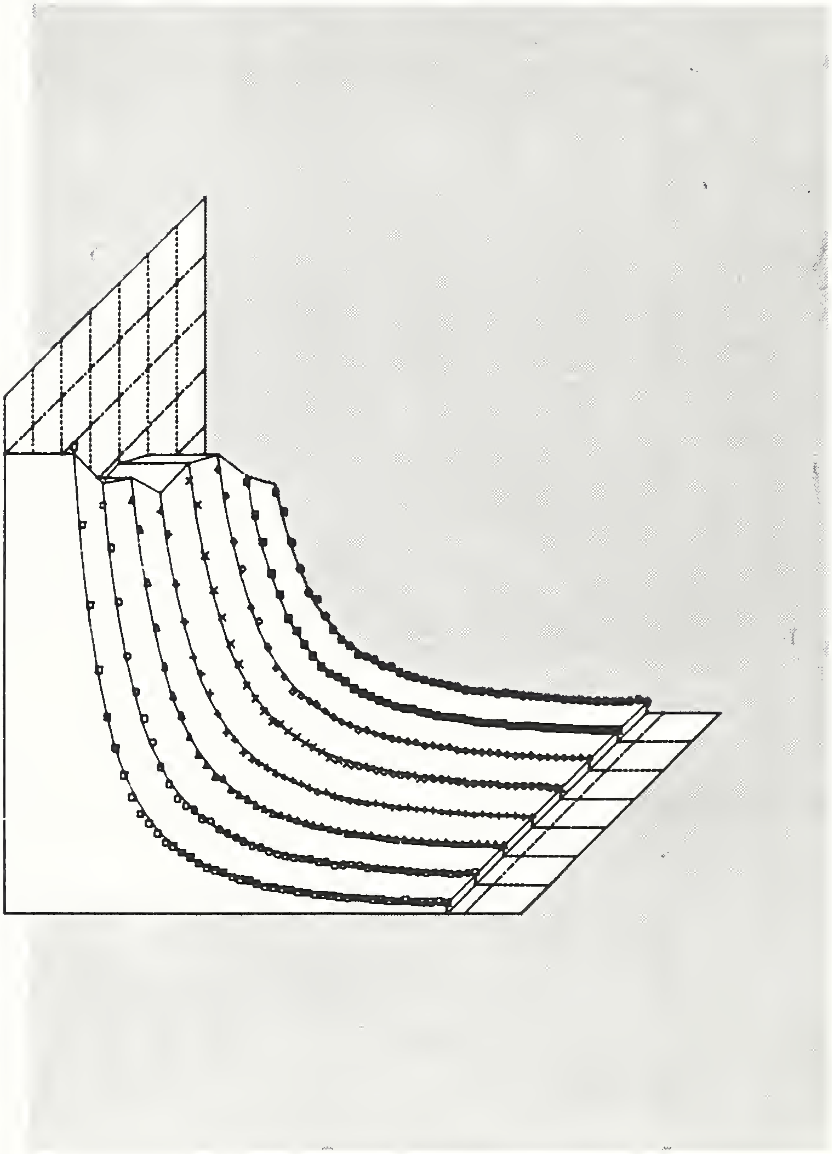
POLYMERS



NAS-NRC
Assessment Panel
February 1–2, 1990

NISTIR 89-4150
U.S. Department of Commerce
National Institute of Standards
and Technology

Technical Activities 1989

neutron scattering lend of deuterated and poly (vinylmethylether) at constant temperature as a function of shear rate. Data shown is the scattering intensity parallel to the flow direction versus the scattering vector. The curves show data at zero shear (front) and at increasing shear rates to 100 sec^{-1} (rear). The decrease in scattering intensity indicates shear-induced mixing. Studies of this type are important for understanding the effects of shear on the miscibility behavior of polymer blends and correlating the morphology of polymer blends with processing conditions.

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POLYMERS

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

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Polymers Division

LESLIE E. SMITH, Chief. Dr. Smith was born in New York. He earned degrees in chemistry from Case Institute of Technology and Catholic University. Except for a three year period of graduate study, he has been with NBS since 1964.

BRUNO M. FANCONI, Deputy Chief. Dr. Fanconi was born in Merced, California. He earned degrees in physical chemistry from the University of California at Los Angeles and the University of Washington. He joined the staff of NBS in 1971.

MARTIN G. BROADHURST, Assistant Chief. Dr. Broadhurst was born in Washington, D.C., and earned degrees in physics at Western Maryland College and Pennsylvania State University. After teaching at Pennsylvania State, he joined NBS in 1960.

G. THOMAS DAVIS, Group Leader, Electrical Properties. Dr. Davis was born in Montour Falls, New York. He earned degrees in chemical engineering at Cornell University and physical chemistry at Princeton University. Prior to joining NBS in 1964, he worked for Esso Research and Engineering Co. and taught at the University of Virginia.

DONALD L. HUNSTON, Group Leader, Polymer Composites. Dr. Hunston was born in Springfield, MI. He earned degrees in mathematics and chemistry at Kent State University. Prior to joining NBS in 1980, he was a Postdoctoral Fellow at Northwestern University and worked in the Chemistry Division at the Naval Research Laboratory.

CHARLES C. HAN, Group Leader, Polymer Blends. Dr. Han was born in Szuchuan, China. He earned his B.S. in chemical engineering at National Taiwan University, M.S. in physical chemistry at the University of Houston and his Ph.D at the University of Wisconsin. He joined the staff of NBS in 1974.

FRANCIS W. WANG, Group Leader, Chemical Performance and Standards. Dr. Wang was born in Peikang, Taiwan. He earned the B.S. and M.S. in chemical engineering at California Institute of Technology and the Ph.D. in physical chemistry at the University of California, in San Diego. He joined the staff of NBS in 1972 after a postdoctoral period at the Polytechnic Institute of New York.

JOHN A. TESK, Leader, Dental and Medical Materials. Dr. Tesk was born in Chicago, Illinois. He holds the degrees of B.S., M.S. in Metallurgy and Ph.D. in Materials Science from Northwestern University. Prior to joining NBS in 1978, he was at the University of Illinois, Chicago, on the staff at Argonne National Laboratory, Director of R&D with the Dental Division of Howmedica, Inc. and Director of Education Services at IGT.

BRUNO M. FANCONI, Group Leader, Mechanical Performance.

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INTRODUCTION

POLYMERS DIVISION

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

The Polymers Division is responsible for providing standards, measurement methods, and fundamental concepts of polymer science to assist U. S. industries that produce or use synthetic polymers in essential parts of their business. This broad mission does not change markedly with time but the specific technical programs within this broad mission must be continually assessed to meet the industry's changing priorities.

This year we expanded our program in polymer matrix composites. While these materials have been used for some time as high performance laminates for the defense and aerospace industries, their use in a wider variety of civilian markets has been inhibited by several technical factors. An important barrier is that the low volume lay-up processes used to make very high performance aerospace parts cannot be easily adapted to higher production volumes and lower part costs. There is a need to provide a science base for composite processing methods that have broader potential applications to civilian transportation, machinery, electronics, and construction markets.

Following the recommendations of industry representatives, our program emphasises study the behavior of polymers in transfer molding or reaction injection molding processes. Preliminary work on modeling such processes is described in this report. Flow visualization experiments will be carried out during the coming year to provide data to verify and refine such models.

A second barrier to the more widespread use of polymer composites is our limited ability to measure and understand the way these materials perform or fail in service. The highly anisotropic properties that allow composites to be tailored for a specific application make their failure behavior very complex. Composite properties are also highly dependent on their processing conditions. This means that a meaningful composites program must integrate the mechanics of composites with an understanding of the materials science of the polymer matrix, the fibers, and the influence of process conditions. This is the goal of the next phase of the program.

Technology transfer to industry continues to be a major concern of all of the Division's programs. The most effective method 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. Last year the Division cooperated with over 130 Research Associates and Guest Scientists who together spent 50 staff years of effort at our laboratories. In addition, many industrial scientists have spent one or two days using specialized equipment developed by Division scientists to explore future research collaboration or to make proprietary measurements on their developmental materials.

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 & SOLUTIONS
DENTAL AND MEDICAL MATERIALS

These Groups have made a number of significant accomplishments during the last year. Some of these are summarized below.

- A program of technology transfer with duPont has been initiated for the study of functionally terminated macromonomers. Copolymerization of macromonomers with conventional monomers has been studied and the resulting copolymers have been evaluated as radiation cured ink resins. The influence of macromonomers on the compatibility of crosslinked polymer networks has been explored by small angle neutron scattering.

- In a cooperative program with Union Carbide, the thermal pulse technique for measuring charge distribution in polymer films has been successfully applied to characterize charge accumulation in films especially prepared for electrical insulation.

- Highly polarizable molecules with potentially nonlinear optical properties have been incorporated into poled films of vinylidenefluoride-trifluoroethylene copolymers. Subtle changes in optical absorption spectra have been analyzed to assess internal electric fields and more dramatic changes in spectra indicate field-induced degradation of the copolymers.

- In collaboration with scientists at the Naval Surface Warfare Center, an optic-fiber fluorescence sensor has been installed at the exit die of a twin screw extruder. The sensor has been successfully used for in-situ monitoring of residence time distribution, quality of mix, and flow instabilities.

- A pyrite reference material was produced, providing a standard substrate for academic and industrial testing of ore leaching bacteria.

- A new constitutive relationship which significantly improves the agreement of predictions of the widely used BKZ formulation and experimental results has been successfully used to interpret the creep recovery behavior of linear low density polyethylene of the sort used in natural gas distribution systems.

- Infrared dichroism measurements have shown that the response of the molecular networks in epoxies to deformation is predominantly an unfolding mechanism. This is consistent with previous results from small angle neutron scattering measurements. Such results are critical to optimizing the mechanical properties of thermosets and hence their composites.

- A previously developed technique to measure the resistance of polymer resins to interlaminar crack growth in their composites was extended to the shearing fracture modes. The test uses a thin adhesive bond between metal adherends to simulate the constraint on the resin deformation produced in the composite by the fibers. Results show excellent correlations between the shearing fracture energies obtained in the adhesive joint test and the composite measurements.

- Phase diagrams of polymer solutions and melts under shear were measured using a specially constructed couette geometry shear cell. For a polystyrene and polybutadiene blend dissolved in dioctyl phthalate, a depression of the spinodal temperature was observed for all shear rates examined. The results indicate shear induced mixing and are in qualitative agreement with results obtained by other methods.

- The 10-meter SAXS Facility had active outside users which includes 4 industrial laboratories, 3 academic institutions, and 3 activities involving other federal laboratories. Activities of users include: studies on the effect of processing conditions on the final state of polyethylene films, studies of the relationship between the amorphous and crystalline phases in semicrystalline polymers, and studies of the effects of compression deformation on the fibers in a composite.

- Blends of linear protonated polystyrene and crosslinked deuterated polystyrene have been studied by small angle neutron scattering. It was found that linear chains can be incorporated into networks formed by sequential polymerization of the network surrounding the linear component (i.e. single phase blend of linear and crosslinked polymers) if the network density is kept low. This result helps to explain why similar systems studied in the past at higher crosslink densities have almost always phase separated at some point during the synthesis.

- The tracer diffusion coefficient of anthracenophane has been measured in various polymer matrices (polystyrene 422K, 2.8K, poly(vinylacetate), poly(vinylmethylether), polystyrene 422K with trace solvent) over a wide temperature range. The temperature dependence of the dye diffusion coefficient is found to be universal once the diffusion coefficient in each polymer matrix is scaled to the diffusion coefficient at the reference state of the glass transition temperature of the polymer matrix. A significant annealing effect on dye diffusion has been observed near the glass transition temperature, which is attributed to slow rearrangement of the polymer matrix.

- A patent was applied for on the use of microwave generated gas plasmas for sterilization of dental and medical instruments in as short as 1-2 minutes at temperatures near or below 60°C.

- Multifunctional oligomers which polymerized by cyclopolymerization yielded highly crosslinked polymers with high degrees of conversion. Favorable results were obtained when they were substituted for BIS-GMA in dental composite formulations.

RESEARCH STAFF

Antonucci, Joseph M.	o Synthetic and polymer chemistry o Dental composites and cements o Antioxidants
Barnes, John D.	o Gas and vapor transport in polymers o X-ray scattering o Computer applications in polymer measurements
Bauer, Barry J.	o Polymer synthesis o Neutron, x-ray and light scattering
Blair, William R.	o Ultratrace metals speciation o Biotransformation of metals o Polymer analysis by size exclusion chromatography o Environmental durability of coatings
Blosser, Richard L.*	o Adhesion measurements
Bowen, Rafael L.*	o Adhesion o Dental composites o Biocompatibility
Brauer, Gerhard M.[†]	o Synthetic and polymer chemistry o Dental composites and cements o Adhesion o Orthopedic materials
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

*Research Associate
†Guest Scientist

Broadhurst, Martin G.	o Dielectric measurement o Piezoelectric and pyroelectric modeling and theory o Equation of state of polymers o Ionic conduction
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	o Computational mechanics (finite element analysis) o Strength of materials o Engineering mechanics of polymer based materials
Chen, Yihong†	o Mechanical behavior of polymers o Rubber elasticity

*Research Associate
†Guest Scientist

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
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
DeReggi, Aime S.	o Polarization-depth profiles in polymers o Space charge in dielectrics o Ferroelectric polymers o Polymeric piezo- & pyroelectric devices
de Rijk, Waldemar G.	o Clinical dentistry o Ceramic materials o Expansion characteristics of solids and semi-solids o Weibull analysis o Gas plasma sterilization
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

*Research Associate

Duran, Randolph S.	o Polymer liquid crystals o Physics of polymer glasses
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
Fanconi, Bruno. M.	o Infrared & Raman spectroscopy of polymers o Structure of polymers o Polymer fracture o Process monitoring of polymer composites
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
Gregory, Thomas M.*	o Calcium phosphate compounds o Surface chemistry
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
Han, Charles C.	o Phase behavior of polymer blends o Phase separation kinetics of polymer blends o Polymer characterization o Polymer diffusion o Small angle neutron scattering o Static and quasi-elastic light scattering

*Research Associate

Hailer, Arthur W.*	o Chemical reactions, chemical analysis
Hunston, Donald L.	o Adhesion science and technology o Fracture behavior of polymers o Processing & failure behaviors of polymer composites o Flow behavior of dilute high polymer solutions o Macromolecule-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
Keeny III, Spurgeon M.	o Gas plasma sterilization o Mechanical testing o Tribology, 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

*Research Associate

Kim, Hongdoo	o Polymer diffusion o Forced Rayleigh Scattering o Polyelectrolyte o Polymer Blends
Kirkpatrick, Diana M.*	o Adhesion o Chemical analysis
Kotowski, Kristine S.	o Synthesis of chromophore-labeled polymers
Krueger, Susan T.	o Macromolecular structure o Small angle neutron and x-ray scattering o Dynamic light scattering o In-vivo characterization o Organic and inorganic composite particles
Kryder, Samuel J.	o Electronic circuit design & construction o Electronic troubleshooting & repair
Lee, Andre	o Infrared & fluorescence spectroscopy of polymers o Statistical physics of polymers o Mechanical behavior
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
Mathew, Mathai*	o Crystallography o Calcium phosphate compounds
Maurey, John R.	o Ultracentrifugation o Rayleigh light scattering o Osmometry o Densimetry o Refractometry o Intrinsic viscosity

*Research Associate

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 o Rubber elasticity
McKinney, John E.†	o Tribology 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 Viscoelasticity of adhesives
Mopsik, Frederick L.	o Dielectric measurements and behavior o Automated measurement design o Computerized data analysis & programming o Electrical properties of polymers
Muller, Robert*	o Denture base materials o Soft liners
Nakatani, Alan	o Polymer blends and solution properties under shear o Small angle neutron scattering o Phase behavior of polymer blends
Olson, Gregory J.	o Metals biotransformation o Bioprocessing industrial materials o Epifluorescence microscopy imaging o Surface modification and bioadhesion
Parks, Edwin J.	o Macromolecular organometallic chemistry o Metals imaging in coatings o Biological transformation of carbohydrate materials o Archival preservation

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†Guest Scientist

Phelan Jr., Frederick R.	o Resin transfer molding: modeling and processing studies o Viscoelastic flow modeling o Engineering rheology
Reneker, Darrell H.	o Crystallographic defects in polymers o Polymer structure o Electron microscopy of polymers o Vibrational spectroscopy of polymers
Roth, Steven C.	o Piezoelectric polymer transducers-fabrication and applications o Vacuum deposition of metals o Calibration of polymer transducers o Microcomputer interfacing
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
Schen, Michael A.	o Living polymer synthesis o Polymers for non-linear optics o Molecular electronics o Optical spectroscopy
Schreiber, Carol T.*	o Topical dental fluorides
Sieck, Barbara*	o Calcium phosphate compounds o Chemical analysis
Smith, Leslie E.	o Adsorption of polymers o Polymer degradation reactions

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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
Takahashi, Yoshiaki †	o Polymer Rheology o Block copolymer o Polymer synthesis and characterization
Tesk, John A.	o Bond strength characterization o Casting of alloys o Strength of dental systems o Thermal expansion & 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
Trout, Todd K.	o Photoactive organometal-chelate chemistry o Diffuse reflectance/microscopic epifluorescence o Spectrophotometry o Element-specific microscopic epifluorescence
Tung, Ming, S.*	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 1-10 nm scale o Structure of asphalt cements
Venz, Sabine*	o Clinical dentistry o Dental composites o Dental polymers

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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 Micro analytical techniques
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
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 & Rheology o Non-linear mechanical behavior of polymers o Static fatigue of plastics o Finite elasticity (rubbers)

*Research Associate

SPECIALTY POLYMERS

The task of the Specialty Polymers Group is to characterize the properties of polymers for special applications, develop new measurement techniques when needed, as well as to synthesize new polymers directed toward specific applications. Much of the effort involves the interaction of electric fields with polymers in which the properties measured are dielectric constant and loss, distribution of charge or polarization, piezoelectric and pyroelectric activity, and electro-optic activity. Polymers being synthesized for particular applications include resins for intaglio printing inks which dry in air as well as resins for inks that will be crosslinked in an electron beam. Polymer systems designed to have non-linear optical properties are being prepared as well as hybrid systems in which NLO molecules are dispersed in electrically oriented polymer films.

The measurement of dielectric constant and dielectric loss as a function of frequency and temperature has long been used to probe the molecular motions in polymers. Development of a time domain dielectric spectrometer at NIST has extended the ability of these measurements to follow dielectric properties which evolve with time, since data for a wide frequency range can be obtained in an interval of time comparable to the reciprocal of the minimum frequency of interest. For example, dielectric data have been used to monitor cure of thermosetting resins, to characterize effects of combined heat and gamma radiation on electrical insulation, and to characterize the state of firing of ceramic materials.

The measurement of charge and polarization distribution in polymer thin films using a laser-induced thermal pulse continues to be indispensable in a variety of programs. The effect of injected charge on altering internal electric fields in DC cable insulation has been assessed and currently, the quantity and distribution of charge is being measured to correlate with the tendency for tree formation in polymer electrical insulation. The principle of non-uniform displacement of polymer and its associated charge is being extended to a pressure pulse generated by the laser-induced ablation of an electrode which will allow examination of much thicker specimens.

Experience and knowledge gained from our research into piezoelectric and pyroelectric polymers continues to be of assistance to commercial enterprises interested in developing applications for these polymers. In addition, it is helpful in our own research on the electric field induced orientation of molecules for nonlinear optical effects. Molecules with known non-linear optical properties can be dissolved in electrically oriented polymers and become preferentially aligned in the internal field of the polymer. Subtle changes in the optical absorption spectra of the dissolved molecules reflect the internal field to which they are exposed. Changes in spectra large enough to be evident as a color change have also been observed. The large changes are believed due to protonation of the dissolved molecules by HF liberated from the vinylidenefluoride copolymer when subjected to high electric fields.

Highly conjugated polymers have been shown to exhibit many properties desirable for use in nonlinear optics (NLO). These include large third order electro-optic coefficients, picosecond response times, and resistance to laser damage in the energy range of interest. Research within the group centers on substituted diacetylene monomers which polymerize in the crystalline or liquid crystalline phase. Goals of the research are to understand the molecular architecture necessary for large nonlinear optical properties and to test the feasibility of controlling the morphology of the usually intractable polymer through the organization of the monomer phase before polarization. The dissolution and subsequent electric field-alignment of NLO molecules in a polymer matrix is also being investigated.

Our expertise in polymer synthesis and characterization is being applied to a program sponsored by the Bureau of Engraving and Printing to understand the characteristics required of a resin base for intaglio ink printing. The requirements for air-dry inks in the printing of U.S. currency are unique within the printing industry. For example, resins which must eventually resist harsh environments such as hot soapy water must be dispersible in these same solutions during the printing process. Alkyd resins based on esterification of polyhydric alcohols with linseed oil fatty acids to provide crosslinking in air and acid anhydrides to provide initial dispersibility in water have shown the most promise.

A cooperative program with duPont has been initiated in which copolymerization studies of functionally terminated macromonomers with conventional monomers will be studied. A portion of these studies have been incorporated in the BEP program to synthesize printing ink vehicles which can be cured with an electron beam. The most effective resins for this application are acrylates and methacrylates and it is hypothesized that incorporation of a macromonomer in the resin will reduce the quantity of the potentially toxic acrylates and methacrylates required for good quality inks. The role of these macromonomers in stabilizing polymer blends of which they are a component is also being studied by small angle neutron scattering.

FY 89 Significant Accomplishments

- Time domain dielectric spectroscopy has been applied to characterize resins to be used in radiation dosimeters in a project sponsored by the Federal Emergency Management Administration.

- From a series of alkyd resins based on esterifying polyhydric alcohols with drying oil fatty acids and acid anhydrides, two have passed preliminary tests at BEP for use as intaglio ink resin vehicles.

- A program of technology transfer with duPont has been initiated for the study of functionally terminated macromonomers. Copolymerization of macromonomers with conventional monomers has been studied and the resulting copolymers have been evaluated as radiation cured ink resins. The influence of macromonomers on the compatibility of crosslinked polymer networks has been explored by small angle neutron scattering.

- In a cooperative program with Union Carbide, the thermal pulse technique for measuring charge distribution in polymer films has been successfully applied to characterize charge accumulation in films especially prepared for electrical insulation.

- Highly polarizable molecules with potential nonlinear optical properties have been incorporated into poled films of vinylidenefluoride-trifluoroethylene copolymers. Subtle changes in optical absorption spectra have been analyzed to assess internal electric fields and more dramatic changes in spectra indicate field-induced degradation of the copolymers.

AUTOMATED DIELECTRIC MEASUREMENTS

F. I. Mopsik

The Time-Domain Dielectric Spectrometer has maintained a high level of activity this current year. The instrument, which was developed at NIST, carries out measurements in the frequency range from 10 kHz to 0.0001 Hz by measuring the charge response of a dielectric to an applied voltage step for times from 10 μs to 3000 s and performing a numerical transform on the data. The sensitivity, accuracy and extremely wide frequency range has led to the commercialization and sale of the instrument by IMASS, Inc. Hingham, MA.

The measurement capabilities have led tc the application of the technique to a wide variety of problems. These have included process monitoring, lifetime studies and material suitability. In addition, to preserve the usefulness of the instrument and broaden its applicability, the updating of the digital hardware and programs has begun.

Instrumentation

The spectrometer, developed originally on an Interdata 7/16 minicomputer for control, acquisition and computation, is being modernized by for the newly developed capabilities of PC compatible computers. The new computer will not only ensure the continued lifetime of the instrument and provide enhanced measurement range, but also significantly expand the capabilities to control a measurement sequence. It is ultimately expected to have the computer control not only the measurement but also the sequence of the data collection and sample environment. Furthermore, the experiment should be able to be carried out in a background mode so that data analysis can be done while new data is being collected.

This year a new computer and acquisition cards have been acquired. Revised instrumentation interfaces have been designed so that the current equipment can be plug-compatible with the new computer. The process has also begun to bring over the previously developed software and make it compatible with the new computer. Extensive modifications have to be made to provide for real-time screen graphics, upgrading from old FORTRAN IV, and interactions with both the new interface boards and the operating system. While this activity is being carried out, the original computer system is being kept active so that no measurement capability is lost.

Process Monitoring

In addition to activities described under the Polymer Composites Group, dielectric measurements were pursued to monitor processing in the production of ceramics. In this joint venture with the Ceramics Division several samples of alumina ceramic have been examined at different firing conditions. Measurements have revealed that not only can the presence of pores be determined, but also that the change in grain boundaries can also be followed. This work is being pursued and it is expected that more definitive results can be obtained.

Reactor Cable Insulation Testing

In a joint project with the Electrosystem Division sponsored by the Nuclear Regulatory Commission research is directed toward evaluating test methods for estimating the useful lifetime of cable insulation subjected to radiation within the confinement area of a reactor. Previous work had shown that dielectric loss at low frequency was much larger in cable insulation removed from service than in the same cable which had been stored outside the reactor. The sensitivity of dielectric loss to radiation was confirmed this past year in a series of polyethylene-insulated cables which had been subjected to controlled doses of radiation at room temperature as well as at an elevated temperature. For the cables studied, the addition of antioxidants suppressed radiation damage. A controlled set of cables are now being exposed to increasingly larger radiation doses under controlled conditions for further dielectric measurements to be correlated with other measures of insulating integrity.

Material Evaluation

The Federal Emergency Management Agency (FEMA) sought assistance in the evaluation of polystyrenes to be used in the construction of radiation dosimeters. It is important that the electrical leakage characteristics of the polymer not be altered after short exposure to high levels of ionizing radiation. The leakage characteristics tend to be dominated by adventitious impurities introduced during polymerization, or subsequent processing rather than being an intrinsic property of the polymer. The high sensitivity of dielectric loss measurements had enabled selection of materials with the appropriate electrical characteristics before exposure to ionizing radiation. These materials are now being irradiated for further evaluation.

Polymer Electrets

A sample of poly(vinylidene cyanide, vinyl acetate) was investigated for dielectric relaxation in order to evaluate its behavior as an amorphous glassy polymeric electret. It has the promise of having higher temperature capabilities than polyvinylidene fluoride. The data showed that there were two relaxation regions associated with the subglass and glass relaxations. What was especially noteworthy was the finding that at 150°C, the response was completely dominated by a pure conductance term but that by increasing the temperature to 175°C, the glass relaxation shifted to sufficiently short times that it could be separated from the conduction loss. These data show that the motions involved in overall rotation have a much higher apparent activation energy than the motions associated with ionic conduction. With a dispersion amplitude of over 100, this suggests that the polymer must have some rigid rod character.

ELECTRIC CHARGE AND POLARIZATION DISTRIBUTION

A. S. DeReggi

The thermal pulse technique continues to be useful for measuring the charging characteristics of polymers under an applied dc voltage (poling) and the discharging characteristics after the applied voltage is removed.

In a cooperative project with the University of Connecticut, and Detroit Edison, measurements have been performed of the space charge induced by poling in five crosslinked polyethylene (XLPE) samples cut from ac cables aged for different time intervals in the range 0-1200 days. The ac aging conditions involved the application of a field of 6 kV/mm at 60 Hz at 90°C for a daily load cycle consisting of 8H on followed by 16 H off. Two of the cables were dc tested from time to time during the ac aging history. The main aims of the measurements were to determine whether or not ac aging can be monitored by measuring the charging characteristics and whether or not dc testing has lasting effects which can be detected in the charging behavior. Members of the power cable community concerned with failure analysis have observed that dc tested cables seemed to fail more frequently than cables with similar aging histories which were not dc tested.

Thermal pulse measurements made shortly after poling showed that the amount of charge which was induced by poling is a monotonically increasing function of the ac aging time. The measurements did not show a significant difference of behavior for the dc-tested cables. Thermal pulse measurements were repeated periodically after poling to monitor the decay of the poling induced charge in all the samples. These measurements showed that the relaxation time characterizing the discharge is of the order of a week. This information is valuable in that the power cable industry sets guidelines for returning ac cables to full operating voltage after the voltage has been removed for testing or other manipulation. These guidelines are based on the assumption that cables relax electrically much more rapidly than observed in the present work.

In another cooperative project, this one involving the Union Carbide Corporation and one of its consultants, Martin G. Broadhurst, a guest worker in the Polymers Division, the thermal pulse technique is applied to the study of water trees in polymeric insulation in underground coaxial power cables. Water trees are erosion channels that spread through the polymer insulation under the combined effects of water and electric field and seriously shorten the cable lifetime. The charging characteristics of insulating materials of known tree resistance are being measured to seek a correlation with tree resistance.

The first part of the program calls for making charging measurements on samples poled under dry conditions (i.e., in the humidity-controlled environment of the laboratory), at 60°C, using fields up to 40 kV/mm. In these measurements, distinct differences are observed in the charging behavior of a commercial, tree-resistant, ethylene-propylene rubber (EPR) compound when compared to that of a conventional polyethylene (PE) not treated for tree resistance. The PE shows negative charge distributed nearly uniformly across the entire thickness with only a very narrow layer of positive charge against the electrode which was positive during poling. The amount of remanent charge in the PE is proportional to the poling voltage. The magnitude of the electric field produced by the remanent charge at each electrode is nominally 10 percent of the poling field. While the EPR also shows negative charge with a broad distribution starting from the electrode which was negative during poling and extending across nominally half the thickness, it shows also positive charge with a broad distribution starting from the electrode which was positive during poling and extending across nominally the other half of the thickness. Moreover, the magnitude of the field at the electrodes due to the remanent charge is twice that for PE. Unexpectedly, it was found that the EPR is slightly pyroelectric. Since pyroelectricity can lead to increased dielectric loss, the component responsible for the pyroelectricity is being sought.

The second part of the program calls for making charging measurement on samples poled under conditions which simulate the service environment. For this purpose, a poling arrangement is under development where one surface of the samples is exposed to an aqueous solution of sodium chloride with molar concentration in the range 0.01 to 0.05 M. The saline solution serves as one of the poling electrodes.

During April and May 1989, a member of the Specialty Polymers Group, A. S. DeReggi, was an Invited Professor at the Ecole Superieure de Physique et de Chimie Industrielles (ESPCI) in Paris, France where the pressure pulse method of measuring charge distribution was pioneered. This method is the acoustic counterpart of the thermal pulse method developed at NIST. In the pressure pulse method, an acoustic pressure pulse is used to produce a propagating inhomogeneous deformation in the sample across its thickness. In the thermal pulse method, one dimensional heat flow produces a diffusive inhomogeneous deformation. In both cases, it is the electric response to the inhomogeneous deformation which carries information about the charge distribution in the dielectric. The acoustic pressure pulses are generated by laser ablation of an absorbing coating on the surface of the sample. This coating is usually applied over the metallic thin film electrodes. In the thermal pulse method, the normal absorption of a laser pulse by the metallic electrode is sufficient to generate the required electrical response.

In collaboration with scientists at the ESPCI, Dr. DeReggi made survey pressure pulse measurements on a variety of samples which were previously studied at NIST by means of the thermal pulse method. The main purpose of these measurements was to compare the acoustic and thermal pulse methods. Samples measured included PVDF, PVF, P(VDF-TrFE), P(VDF-TFE), PVC, PE, a commercial ionomer, and PZT ceramics. These samples represent a range of acoustic and thermal properties as well as a range of thickness. From these measurements, it was concluded that the two methods are complementary. The acoustic pulse method is best suited to measure charge imbedded deeply in the bulk of a relatively thick (1 mm or more) sample while the thermal pulse method is best suited to measuring polarization in relatively thin samples (100 μm or less). In most polymers, the high frequency dispersion properties are such that to gain the most information from the pressure pulse method, deconvolution is necessary just as it is for the thermal pulse case.

In addition to the survey measurements, extensive measurements were performed on electron-beam charged as well as on voltage poled PVC and on voltage poled PZT. The PVC measurements were done not only at the ESPCI but also at ONERA (the French equivalent to NASA) where facilities were available to expose a sample in vacuum to an electron beam of energy up to 40 keV and to measure its pressure pulse response without breaking vacuum. These measurements confirmed the earlier observation at NIST of radiation-induced polarization of PVC below its glass transition temperature, Tg. Pressure pulse measurements on voltage-poled PVC samples as a function of temperature showed observable polarization only for samples poled near or above Tg.

The pressure pulse measurements on PZT were undertaken with the additional collaboration of the U.S. Naval Research Laboratory (NRL). The purpose of these measurements was to find out if compositional variations induced during processing could be detected through the observation of an inhomogeneous polarization distribution after voltage poling. These measurements showed unambiguously that samples fired in a controlled atmosphere had homogeneous polarizations while those fired in an uncontrolled atmosphere had inhomogeneous polarizations. These results suggest that lack of tight control on ceramic processing variables can lead to composition gradients. Because the useful PZT formulations lie very close to the morphotropic phase boundary separating the cubic from the tetragonal phase, a composition gradient can lead to an observable variation in polarization.

DESIGN AND SYNTHESIS OF INTAGLIO INK RESINS

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

NIST is developing prototype ink vehicles for intaglio printing at the Bureau of Engraving and Printing. Intaglio printing is used only in special cases, so there has been little commercial activity in developing inks for the intaglio process. Many inks cure by solvent evaporation, but the solvent must then be removed from the effluent air stream. For security documents, it is desirable that the inks cure by crosslinking rather than by solvent evaporation. This also helps comply with air pollution regulations. The objective of this project is to provide information on the design and synthesis of resins which are suitable for two types of intaglio inks: those that crosslink on exposure to air; and those which crosslink 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 performance requirements for the resins impose severe constraints. The viscosity of the resin must be in the region of 30 to 200 poises. So that the ink can be removed automatically from the press during printing, the formulated inks, consisting of the resins, pigments and other solids and perhaps solvents, must disperse in 1% aqueous sodium hydroxide to which 1% w/w of surfactant has been added. In addition, the resins must keep the solid ingredients of the ink in suspension and the formulated ink must transfer acceptably from the engraved cylinder to the paper substrate.

Two series of intaglio inks have been developed. The first is based on molecules which are similar to 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. At least one member of each series of resin passed preliminary 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 on exposure to the electron beam. Both methacrylates and acrylates have been used. 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 have more than enough acidity to 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, the resins are so viscous that they must be diluted before they can be used as intaglio ink resins. Although suitable water-dispersible, very low viscosity, electron beam active oligomers are commercially available, there is some concern about the toxicity of these materials, even though they are currently in wide use (much commercial effort has gone into developing low viscosity oligomers). The resins developed at NIST are related to dental resins which have been shown to be sufficiently non-toxic to permit their use in tooth restorations in the mouth. A solvent system for the NIST electron beam resins which is acceptable to BEP personnel must be selected by them and toxicity tests on the neat resins must also be carried out.

MACROMONOMER STUDIES

Barry J. Bauer, Brian Dickens, and R. M. Briber

A program of technology transfer has been initiated with duPont for the study of macromonomers. DuPont has recently developed synthetic techniques for the production of functionally terminated polymers which are capable of copolymerizing with conventional monomers. They have supplied NIST with custom made samples, all being polymethylmethacrylate (PMMA) with terminal alkacrylate, methacrylate, acrylate, alpha-methylstyrene, and unfunctionalized.

One application tested was their use as components in radiation cured ink resins. Mixtures were made of various macromonomers and polyethylene glycol 400 diacrylate. Films with macromonomer content of between 0 and 50% were cured and studied with thermomechanical analysis. The glass transition increased steadily with macromonomer incorporation and the transition became broader. A sample was made from an equivalent polymer, but without the polymerizable group. This sample had two thermal transitions, one near that of a pure network, and one near that of the PMMA indicating phase separation. By controlling the functionality of the PMMA, one can therefore control the morphology of the polymer.

Small angle neutron scattering studies (SANS) were made from polystyrene-d8 networks with polystyrene (PS) and PMMA macromonomers along with controls made with polymers of similar molecular weights as the macromonomers, but without the polymerizable functionalities. Macromonomers were shown to greatly favor compatibility, forming single phase networks where phase separation would normally have occurred. The PS/PMMA system showed a strong peak in the scattering intensity, indicating that samples of this type may microphase separate, causing a morphology within the 100 angstrom range compared with one micron size scale which is typical for conventional phase separated networks.

NONLINEAR OPTICAL MATERIALS

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Polymers containing highly delocalized charge correlated pi-electrons have been shown to exhibit a nonlinear polarization of electron distributions while under the influence of intense electric fields as are associated with pulsed laser radiation. These materials consequently exhibit a light intensity dependent refractive index. It is this property which allows the photonics device engineer to envision electro-optical and integrated optical modulating or switching devices based on such polymers. These types of modulating and switching devices are central to the emerging photonics industry and has application in optical telecommunications, all optical computing and neural networks, image processing, laser research, and laser protection of military equipment and personnel.

It is convenient to categorize nonlinear optical, NLO, polymers into two types of materials, depending upon whether second order, χ^2, or third order, χ^3, hyperpolarizabilities dominate as the materials nonlinear response. To enhance each of these responses, two architecturally different molecular structures have independently emerged. The first, or χ^2 materials, are typically side-chain copolymers containing intramolecular conjugated donor/acceptor molecules, such as 4-amino-4'-nitro stilbene or azobenzene, as the NLO active component and then aligned to give a non-centrosymmetric macroscopically oriented film that contains a permanent preferential transition dipole moment. Alternatively, these same low molar mass moieties are incorporated into a preexisting polymer giving molecular blends or guest-host materials.

The second, or χ^3 materials, are typically semi-conducting, electroactive polymers whereby the NLO response is due to electron delocalization along the polymer backbone. Typical examples include the polydiacetylene (PDA) family of polymers and rigid-rod like polymers such as poly(p-phenylene-benzobisthiazole) or PBT. Research within our group has been involved with aspects of both classes of materials.

A. Second Order Materials

Common to all second order NLO materials is the need to obtain non-centrosymmetric thin films whereby a preferential orientation of the transition moment associated with each individual NLO-active moiety remains. Orienting these dipoles is typically achieved through electrostatic poling procedures similar to those employed with ferroelectric polymers such as poly(vinylidene fluoride) or its copolymers with trifluoro-ethylene. Consequently, an in-depth understanding of the actual poling procedure, the molecular parameters which affect the orientational stability of the poled film, and characterization of the orientational distribution of poled films all become very necessary for fully controlling this aspect of χ^2 material processing.

Within this past year, guest/host films containing small amounts of χ^2-active dimethylamino-nitrostilbene, DANS, or 4-amino-4'nitroazobenzene as the guest and poly(vinylidene fluoride-co-trifluoroethylene) as the host were prepared. Studying the changes in the optical absorption spectra has allowed an assessment of the magnitude of the remanent internal electric field arising from the poled piezoelectric polymer. Also, the influence of the remnant internal field on the orientational stability of the oriented low molar mass χ^2 dye was examined. At temperatures below the Curie transition of the poled polymer, dye orientation appears to be very stable even though the T_g of the polymer amorphous phase, within which the dye resides, is below ambient temperature(see also discussion of ferroelectric materials). Similar studies are now underway examining amorphous films of highly polar polymers.

B. Third Order Materials

For all-optical signal processing, χ^3-active conjugated polymers need to be processed into a waveguide geometry whereby the transition moment of the χ^3-active segment is uniaxially oriented coincident with the propagating electric field vector from the laser pulse. Given that many of the more interesting classes of polymers for third order phenomena, such as conjugated polymers like polydiacetylenes or rigid rod and ladder polymers like PBT, are generally insoluble or marginally soluble at best, processing these materials into low optical loss structures with the desired nonlinear properties becomes a non-trivial task. Our activities in this field have focused on new approaches towards obtaining oriented films of polydiacetylenes. This is based on a series of novel liquid crystalline, (lc), and non-liquid crystalline symmetric diacetylene monomers which incorporate the benzylidene aniline moiety as the mesogenic unit.

As potential elements within NLO devices, PDAs combine a large number of important primary and secondary properties which include a large non-resonant χ^3, picosecond scale switching times, phase matching, and film flexibility to name a few. Because the polymerization of diacetylene monomers is believed to demand nanometer organization of the monomer - traditionally provided by the crystal lattice - exotic procedures to grow large area single crystals of the monomer and conduct a solid state conversion to the polymer have evolved for obtaining large area films. Alternatively, reprecipitated thin films of soluble polydiacetylenes have also been investigated, involving principally the polymer from 4-BCMU(1,12-bis-[butoxycarbonylmethylurethane]-5,7-dodecadiyne) monomer. Though advantages are gained in the processing of these materials into waveguides over insoluble PDAs, electronic defects are introduced into the polymer during dissolution in the form of main chain kinks, bends, or twists; all of which have a deleterious effect on the sub-nanosecond switching times and overall χ^3.

Our work has concentrated on the polymerization and polymer characteristics of n-OBOA(bis-oxybenzyideneoctylaniline) where n, which equals either 1 or 4, refers to the number of methylene spacer groups that separate the diacetylenic unit from the mesogenic moiety(Fig. 1). Because of the additional rotational isomeric states associated with the tetramethylene group in the 4-OBOA, this compound does not show monomer liquid crystalline behavior. 1-OBOA, on the other hand, shows smectic polymorphism over nearly a fifty degree temperature range beginning at ca. 135°C.

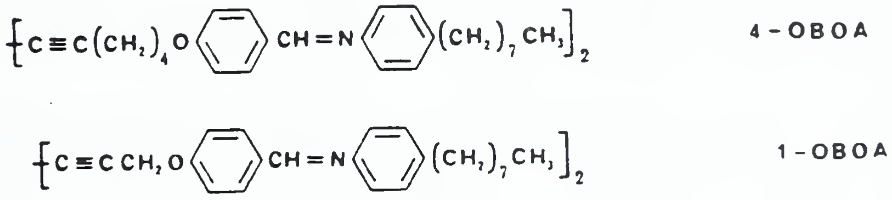

Figure 1

Thermally induced polymerization kinetic experiments of 1-OBOA have uncovered a previously unknown behavior. Within the crystal phase, both 1- and 4-OBOA are essentially unreactive; showing in the case of 1-OBOA an activation energy, E_a, for monomer disappearance of ca. 71 kcal/mol. Heating 4-OBOA above its melting point and into the isotropic phase also shows the monomer to be stable over a period of hours. Heating 1-OBOA into the liquid crystalline region however, corresponds to a drop in E_a to ca. 31 kcal/mol. over the entire lc region. Therefore a phase dependent polymerizability is being observed. Though the intermolecular distances between adjacent diacetylenic residues increases upon traversing the first order crystal-to-liquid crystal transition, the additional mobility of residues within the lc structure allows polymerization to occur.

Heating 1-OBOA beyond its clearing temperature and into the isotropic melt - a state comparable to the melt of 4-OBOA - a broad exotherm is observed by differential scanning calorimetry, DSC, much below the temperature where degradation begins as seen by thermal gravimetric analysis, TGA. Though the energy associated with this exotherm is larger than the heat of polymerization observed for TS(1,6-bis-[4-toluene sulfonate] 2,4-hexadiyne) monomer within the crystal phase, it does appear that this is due to polymerization within the melt of 1-OBOA since an insoluble, optically transparent cherry red film is obtained. Given that the diacetylene unit of 1-OBOA monomer is incorporated within the rigid segment of the molecule, it seems that random collisions of adjacent molecules is sufficient to allow polymerization. 4-OBOA, on the other hand, is a fairly flexible molecule and presumable adventitious collision of the diacetylene segment of the molecule within the melt is prevented. Further work surrounding these points is currently underway.

Small angle and wide angle x-ray scattering, SAXS and WAXS respectively, studies have shown unique features in the polymerization of 1-OBOA. Polymerization experiments conducted within the lc region of the monomer have shown that the layer-like structure characteristic of the monomer appears to be retained in the polymer as evidenced by the appearance of a broad small angle peak at slightly larger d-spacings than the original monomer peak associated with the lamellar structure. However, with conversion, all wide angle reflections diminish in intensity and are virtually nonexistent in the fully converted polymer. These results suggest a one dimensional organized micromorphology in which the polymer chain is confined within a layer but is randomly oriented within that layer. This work is continuing and will additionally focus on scattering behaviors of polymers obtained from the isotropic melt.

The linear and nonlinear optical characterization of polymers prepared within our group are being conducted through a collaboration with Professor Ray Chen of the University of Maryland - Baltimore Campus. Films of melt polymerized poly(1-OBOA) are now being prepared for their evaluation. Aspects under investigation include resonant Raman scattering to evaluate the nature of electronic defects, determination of the linear absorption spectrum and absorptivity, and estimation of χ^3 through third harmonic generation experiments.

As part of our synthetic effort, much improvement has been made in the synthesis of 1-OBOA. What was originally a four step procedure with overall yields of only a few percent has now been improved to a three step synthesis of ca. 75% overall yield. Application of this methodology has now led to the generation of the homologous series of n-OBOA where n now equals 1 through 4. These new materials will prove valuable in observing transitions from lc to non-lc monomer behaviors and insoluble-to-soluble behaviors in radiation polymerized polymers. Also, progress has been made towards the synthesis of our first asymmetric diacetylene monomer whereby the diacetylene backbone is flanked by the rigid mesogen to one side and a flexible alkyl chain on the other. In these materials, the mesogen will also exhibit χ^2 activity. It is anticipated that resulting polymers from these materials will exhibit both second and third order NLO behavior and be soluble in common solvents.

FERROELECTRIC POLYMERS

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The ferroelectric properties of copolymers of vinylidene fluoride and trifluoroethylene continue to be of interest because of the high values of polarization that can be achieved, the variation of the Curie temperature with composition, and the variation of coercive field with thermal history. Recently it was found that the coercive field of these copolymers can be varied from 500 kV/cm for a well crystallized sample to greater than 1 MV/cm for a sample quenched from the melt. Furthermore, the coercive field decreases on the order of 30 percent as the poling field is cycled and increases on the order of 20 percent as a result of storing at temperatures below the Curie temperature. Those variations of ferroelectric properties with electrical and thermal history combined with the variation of Curie temperature with composition can be utilized to fabricate multiple layer films with complex polarization profiles. For example, bi-layer films can be fused together and the two halves poled in opposite directions to create a bimorph which bends upon subsequent application of an electric field. Tri-layer films have been fabricated in which only the center layer is poled but is fused between outer layers which have nearly the same other physical properties.

The large residual polarization in these semicrystalline polymers can be expected to produce large internal electric fields within the polymer film. Others have shown that highly polarizable molecules incorporated within the amorphous regions of the polymer can become preferentially aligned in this field and exhibit nonlinear optical properties such as second harmonic generation. Measurements of small changes in optical absorption spectra of molecules such as dimethylaminonitrostilbene (DANS) and aminonitro-azobenzene (ANAB or Disperse Orange 3) have been conducted to determine the internal fields to which the samples are exposed for various levels of polarization. In this way, internal fields as large as 4×10^6 V/cm are measured in copolymer films with a polarization of 7 $\mu C/cm^2$.

In addition to the small changes in optical absorption spectra of dissolved molecules discussed above, often much larger changes in absorption maxima are observed which could be described as a color change or bleaching. The molecules dissolved in the polymer are dye molecules which could also be acid-base indicators - in fact, the spectral changes observed in the polymer films are similar to changes observed upon acidifying a propanol solution of the dye. It is currently believed that the electric fields employed to orient the copolymer chains have resulted in degradation of the polymer and the liberated hydrogen fluoride is being detected by the dissolved indicator dyes. Further work on this phenomenon is in progress.

CHEMICAL PERFORMANCE

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

The need for improved monitoring of polymer processing has escalated in recent years because of the large demand and market for advanced polymeric materials 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 our 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.

A program was initiated on bioprocessing and molecular characterization of organometallic materials. Investigations in this 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. In addition, in response to the need identified by Congress, a new effort has been initiated to study biodegradation mechanisms of polymers.

FY 89 Significant Accomplishments

- In collaboration with scientists at the Naval Surface Warfare Center, an optic-fiber fluorescence sensor has been installed at the exit die of a twin screw extruder. The sensor has been successfully used for in-situ monitoring of residence time distribution, quality of mix, and flow instabilities.

- A polymeric chromophore, which consists of polybutadiene labelled with fluorescent-active anthracene, has been synthesized and characterized. This polymer has been used to monitor polymeric behavior such as non-Newtonian viscosity and molecular orientation.

- A tagged polystyrene which has a fluorescent dye at the end of the molecule has been synthesized to monitor intersegmental mixing in thermoplastic elastomers.

- Bioleaching of elemental copper in acidic aqueous solutions containing ferric ions has been demonstrated.

- A pyrite reference material was produced, providing a standard substrate for academic and industrial testing of ore leaching bacteria.

- Methods have been successfully applied to characterize metal accumulation and metal particle formation by microorganisms using small angle neutron and x-ray scattering techniques. These methods provide non-destructive techniques for investigating factors affecting the rate of metal processing by microorganisms.

- The use of extremely thermophilic bacteria for coal desulfurization was demonstrated in collaboration with the Johns Hopkins University and with the support of the Electric Power Research Institute. These organisms, by virtue of their rapid metabolic rates, have provided information on the molecular forms of sulfur in coals.

POLYMER PROCESSING

A. J. Bur, F. W. Wang, A. Lee, R. E. Lowry, S. C. Roth, and C. L. Thomas

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. its intensity, polarization, and wavelength distribution, yields information about the state of the polymer matrix. Activities have concentrated on developing concepts and methods to measure molecular orientation, shear stress, shear rate, non-Newtonian viscosity, velocity, flow instabilities, quality-of-mix of ingredients, 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 the measurement of shear stress, non-Newtonian viscosity, quality-of-mix of ingredients, and flow instabilities. In addition, a model for the behavior of the velocity/shear rate probe has been established and a polarity sensitive fluorescent dye has been selected which can be used to monitor intersegmental mixing.

Residence Time Distribution, Quality-of-Mix, and Flow Instabilities

During the past year, the first application of fluorescence monitoring in the processing environment was achieved by installing an optical fiber probe at the exit die of a twin screw extruder. The experiments were carried out in collaboration with M. Galant at the Naval Surface Warfare Center. In this process, a polymer melt (polybutadiene) is combined with solid particulate ($CaCO_3$) at 65% volume concentration, mixed by the twin screw action of the extruder and extruded through the exit die in the form of rod approximately 1 cm in diameter. The objective of the fluorescence monitoring was to observe residence time distribution. A fluorescent dye, coumarin 30, is "instantaneously" inserted into a dye port, which was located 62 cm upstream from the exit die, and fluorescence at the probe point was observed as a function of time. Not only was residence time distribution data obtained, but also flow instabilities, manifested by discontinuities in the fluorescence residence time distribution curve were observed. The flow instabilities were the result of the formation of particulate mats which stopped the flow of material until the machine pressure buildup was large enough to break the mat. Future experiments with this probe will involve correlation fluorescence with pressure and torque data and the measurement of quality-of-mix of ingredients by observing the fluctuations in fluorescence intensity as a function of time.

Shear Stress and Non-Newtonian Viscosity

Our working hypothesis for the anisotropy experiments is that, for a non-Newtonian fluid, the fluorescence anisotropy increases (and the 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 fluorescence probe for these measurements is polybutadiene tagged with fluorescent-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. much larger than its entanglement molecular weight of 3,000.

The apparatus to measure both fluorescence anisotropy and rheological parameters is a cone and plate rheometer which has been instrumented with optical components in order that anisotropy and rheological parameters can be measured simultaneously. Two specimens are presently being examined: low molecular weight polybutadiene with molecular weight of 2800, i.e. less than its entanglement value, and concentrated solutions of polyisobutylene whose molecular weight is much greater than its entanglement value. When the low molecular weight (M_w = 2800) polybutadiene was doped with the tagged polybutadiene (10^{-4} molar concentration), the observed behavior was Newtonian and that its anisotropy was constant in the shear rate range 10 to 80 s^{-1}. It is concluded that, within the sensitivity of our measurement, molecular orientation of the tagged polybutadiene does not occur in this low molecular weight polybutadiene. Without entanglements, stress producing orientation can not be transmitted to the molecular scale. Measurements on the PIB solutions as a function of concentration are continuing.

Intersegmental Mixing

The phenomenon of intersegmental mixing occurs in a two component material which undergoes a transition from phase separated to homogeneous at a critical shear stress. Detection of this transition has application to the processing of block copolymers and polymer blends. Of specific interest to us is the block copolymer styrene-ethylene/butylene-styrene-(SES). In order to detect intersegmental mixing via fluorescence observations a fluorescent dye is selected which has a thermodynamic preference to reside in one of the phases and whose spectrum is sensitive to the polarity or viscosity of its molecular neighborhood. For SES a tagged polystyrene has been synthesized which has a coumarin dye as the end group of the molecule. In the phase separated state, the tagged polystyrene is assumed to reside in the polystyrene phase. Polarity sensitivity has been tested by measuring spectra from model solutions of toluene and cyclohexane doped with the tagged polystyrene. These model solvents were chosen to simulate the polarity effect of styrene (toluene) and ethylene/butylene random copolymer (cyclohexane). The results show a 26 nm wavelength shift in the two spectra which peak at 451 nm for toluene and 425 nm for cyclohexane.

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. ASTM methods operationally define organic sulfur as all sulfur which is not pyrite or sulfate. 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 was 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.

Other recent reports suggest that disulfides or polysulfides may be important forms of "organic" sulfur in coal. It was 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. However, simple model compounds may not be adequate representations of the forms of sulfur in coal, especially with regard to steric factors related to organism/enzyme accessibility. Thus, current research focused on synthesis and testing of polymeric polysulfides may provide a more realistic appraisal of the organisms abilities to attack sulfur in the coal matrix.

Standards for Biodegradation and Bioprocessing

Degradable plastics may be a partial solution to the problem of reducing the amount of plastic wastes in the environment. Regulations are appearing at the state and local level mandating use of degradable plastics. However, there is no clear understanding of the environmental effects of degradation products of such materials, nor are there standard materials, testing procedures, or definitions for degradable plastics. Our research, funded by OSRM, is investigating the feasibility of standards for biodegradable plastics.

During the past year, plastic films were obtained from USDA made of a blend of starch and poly(ethylene-co-acrylic acid). These were exposed to a 5-species population of mixed fungi employing an accelerated testing procedure designed by ASTM committee D-20 to test the resistance of plastic materials to bio-deterioration. After several weeks of incubation, plastic films containing 40% starch or greater were covered with fungal growth, but the films retained their physical integrity. Portions of the films and sterile control films were analyzed by FTIR spectroscopy and by gel permeation chromatography (tetrahydrofuran extracts of films). There was no evidence of biodegradation of the polymer portion of the films (by GPC) and only small reduction in starch was noted by FTIR. Evaluation of additional materials and test organisms is underway.

Another area which is hampered by the lack of standards is in the industrial applications of bioprocessing of coal and metal ores. 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 development of a pyrite ore reference material over the past year. Twenty kg of a New Mexico pyrite was washed, ground, sieved, bottled, sterilized, and packaged under nitrogen with OSRM assistance. The material is being characterized 1) chemically, by x-ray diffraction, x-ray fluorescence and other techniques and 2) microbiologically, by bio-leaching rate. The bio-leaching 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 bio-leaching rates is planned, using the ASTM procedure and the NIST reference material.

New Measurement Techniques for Bioprocessing: Small Angle X-ray (SAXS) and Neutron Scattering (SANS)

Members of our group have had a longstanding interest in the bio-recovery of metals from solution. However, methods are lacking for studying kinetics and mechanisms of metal particle formation without cell disruption and alteration. Metal particles formed in and on bacteria were detected non-destructively using small angle X-ray and neutron scattering facilities in the Polymer Division and at the NIST reactor, respectively. The model system selected was magnetotactic bacteria, which deposit small intracellular crystals of magnetite (termed magnetosomes) in chains. These studies were conducted in collaboration with scientists at the University of New Hampshire. The magnetite particle shape, size and magnetic properties in the intact cells were determined. The particles were ferromagnetic, and slightly elongated along the axis of the magnetosome chains, with a radius a little over 100 Å. Cells grown in a medium containing low levels of iron deposited smaller particles which were super-paramagnetic. In addition, other bacteria were studied which bind platinum, selenium, gallium and uranium. Morphology of the bound metal is being characterized by SAXS and correlated with associated measurements of amount and location of metal using destructive techniques such as atomic absorption spectroscopy and electron microscopy. These scattering techniques show promise for determining mechanisms of metal binding and factors which importantly affect the rate of metal binding by bacteria. Such processes are of interest to industry and governmental organizations exploring methods to recover metals from process and waste streams. In addition, these methods may have applications in biomedical research as techniques for characterizing intracellular metal toxicity.

Steel Research Program

Research under the steel research program concluded in the past year. Previously work centered on novel microbial processes for the beneficiation of iron ore and metal reduction to elemental particles. During the past year experiments investigating selective leaching of copper from simulated copper-steel scrap mixtures were concluded. The presence of copper (e.g., wire) has a deleterious effect on properties of steels made from scrap. It was found that ferric ions in acidic aqueous solution were powerful oxidants of copper and that iron-oxidizing bacteria would continuously regenerate ferric ions from ferrous ions, and maintain the rate of copper dissolution. Moreover, the rate of copper dissolution was dependent on cell numbers. Unless a critical number of bacteria were present in solution (10^9 per ml), the leaching rate of copper coupons did not differ significantly in sterile versus inoculated solutions. Unfortunately, selective attack on copper in the presence of steel could not be maintained, and so the method appears not applicable to copper-steel mixtures. Nonetheless, our demonstration of bio-leaching of elemental forms metals may have applications in bioprocessing of ores or wastes where selectivity of extraction is not critical.

Development of Quantitative Microbial Biosensors for Molecular Topology Prediction of Bioprocessing Routes

In collaboration with Research Associates from Technical Assessment, Inc., a laser bioassay system has been established which measures the effects of toxicants on the angular dependence of scattered light from media containing genetically engineered Bacillus subtilis strains.

We found that the bioassay system could be used to detect sub-micromol levels of several organotin species in water and in complex media. Furthermore, the bacterial test strains, which are genetically identical except in their ability to repair DNA damage, showed differential sensitivities to individual organotin compounds. The results of this study suggest that the bioassay may be useful for speciation of organotins in environmental samples, and may also provide information as to the mode of toxicity and possible metabolic alteration of these compounds.

MECHANICAL PERFORMANCE

The Mechanical Performance Group provides 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 models to describe mechanical response and the elucidation of solid state structure. Work is conducted 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 latter studies support activities in the Polymer Composites Group where the primary focus is on the composite rather than constitutive materials. The development, refinement and utilization of continuum theories which describe mechanical properties are integral aspects of mechanical characterization. Solid state structure characterization uses the more traditional tools of optical and electron microscopy, x-ray diffraction and infrared spectroscopy as well as more recent techniques of solid state nuclear magnetic resonance (NMR) and scanning tunneling microscopy. The potential of scanning tunneling microscopy to elucidate interesting structural features of polymer specimens, including fibers has been evaluated. 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. For example, solid state NMR is used to characterize the molecular organization of asphaltic cements and determine how the structure is affected by temperature and aging in a study funded by the Strategic Highway Research Program. A project with the Department of Transportation aims at developing improved test procedure to assess the compatibility of liquid peroxide ladings with polyethylene packages.

FY 89 Significant Accomplishments

- The aging of polymer glasses subjected to mechanical excitation has been characterized by a torsional dilatometer. This apparatus is used to determine volumetric changes associated with torsional deformation of glassy polymers. Volume recovery data from epoxy resins has elucidated the interrelationships among glass transition temperature, torsional deformation, volume recovery, time and temperature.

- A new constitutive relationship which significantly improves the agreement of predictions of the widely used BKZ formulation and experimental results has been successfully used to interpret the creep recovery behavior of linear low density polyethylene of the sort used in natural gas distribution systems.

- Solid state NMR studies revealed that inhomogeneities in terms of the aliphatic/aromatic compositional ratios exist in one asphaltic cements, but not the other. The dimensions of the inhomogeneities, based on the time required for equilibration of the spin polarization, is larger than 10 nm (as would be expected if micellar structure were present in asphalts).

CHARACTERIZATION OF SOLID STATE STRUCTURE AND MORPHOLOGY

F. A. Khoury, D. H. Reneker, D. L. VanderHart, B. M. Fanconi, G. C. Campbell, Jr., and W. F. Manders

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 the surface of graphite fibers. Details of the structure at the molecular level were investigated with spectroscopic techniques and by molecular modeling, while larger structural features were studied by electron microscopy, optical microscopy, and scanning tunneling microscopy. The morphology of polyphenylene sulphide (PPS) crystallized from solution and the melt has been elucidated in order to better understand the morphology of this high temperature thermoplastic in the presence of carbon fiber reinforcements.

The role of chain entanglements in fiber deformation and resultant fiber properties are elucidated by molecular mechanics calculations which also treat the effect of the lattice and lattice defects.

Solid state NMR is providing information on the structure of asphaltic binders and the evolution of the structure with time and temperature. Such information is useful in understanding the structural origins of rheological properties of asphalts.

Modeling of Entanglements Embedded in Polyethylene

Entanglements play an important role in the drawing of polymer fibers. In the present study the entanglement is treated as a defect in the crystal and the chains are all required to approach their proper lattice sites as the distance from the entanglement increases. This approach facilitates examination of the interactions between the entanglement and smaller crystallographic defects. The smaller defects, by controlling the way chains move through the entanglement, play an important role in the determination of the effects of the entanglements on the properties of the fiber.

A physical model was constructed of a defect that centered around two linked U-shaped chains and two chains that spiraled about one quarter turn around the linked chains. This model of an entanglement contained 5 extra methylene groups in each of the U-shaped chains and one extra group in each of the spiraling chains. This model contained a total of 12 extra methylene groups in a region that would contain 630 such groups on lattice sites, an increase in density of about 2%.

The starting conformation measured from the physical model was adjusted in a supercomputer to minimize the energy. The conformation of single stems or pairs of stems were minimized in succession until a stationary state was reached. The resulting conformation differed from the starting conformation by having a significantly greater preference for conformations close to a planar zig-zag, interrupted where necessary by relatively large rotations around a few successive bonds.

A dispiration, a type of small crystallographic defect that both translates the chain along its axis and rotates the chain 180 degrees around its axis, was placed in the leg of one of the U-shaped chains. The dispiration will be driven into the entanglement to investigate this mechanism for a chain to move through the entanglement.

Scanning Tunneling Microscopy of Polymers

The scanning tunneling microscope was used to examine the morphology of precipitated ultra-high molecular weight (ca. 5 million) polyethylene. A thin layer of hot solution was trapped between two sheets of mica, and then cooled rapidly to precipitate and crystallize the polymer. At the concentration used, 0.001 g/ml, the polymer molecules were entangled sufficiently to affect the morphology of the precipitated material.

The samples were shadowed with a layer of evaporated carbon and platinum and examined with a transmission electron microscope. The free surface of the electrically conducting shadow layer was also imaged with the scanning tunneling microscope. A great variety of morphological forms were observed. These include elongated branched structures, particles with volumes appropriate for a single contracted molecule, lamellar crystals, shish kebabs, smooth fibers, and thin, elongated patches of polymer that could only be seen with the scanning tunneling microscope as a result of its high sensitivity in the vertical direction. Steps in the locally averaged thickness of the elongated branched structures which corresponded to the thickness of single layers of molecules were observed. In some parts of the sample, lines separated by about 0.75 nm, which is the separation in the a-axis direction of the molecules in the [020] planes were seen. These lines have characteristics of the trajectory of the backbone of a single polyethylene molecule, including kinks, bends, curves, crossing, and chains that terminate or leave a particular layer, but all possible confusing artifacts have not yet been eliminated.

This work shows that surfaces of polymer objects coated with a thin conducting layer of platinum and carbon can be imaged with the scanning tunneling microscope in air without the necessity of removing the layer from the surface, as is generally necessary for transmission electron microscopy. The lateral resolution is limited in both cases by uncertainties associated with the platinum/carbon layer, but the scanning tunneling microscope contains much more quantitative information about the height of the sample.

Our review of the application of the scanning tunneling microscope to the examination of polymers and other organic molecules is completed and will be published this year. Recent work in other laboratories indicates that under favorable conditions, the positions of the hydrogen atoms in the alkane tails of a liquid crystal molecule can be observed by tunneling through the molecule into a conducting substrate.

Ordered, Solid-state Forms of Isotactic Polystyrene

This project is aimed at using solid-state ^{13}C cross-polarization (CP) spectra, taken in the presence of magic angle spinning (MAS), in order to detect differences in ordered, solid state structures of isotactic polystyrene (iPS). In work described in the 1988 Annual Report CP-MAS spectra were obtained on iPS in the following forms: a) glass, b) 3_1 helical crystal, c) a gel of 25% iPS in trans decalin, d) cyclooctane vapor-induced (CVI) crystals and e) a vacuum dried gel of 25% iPS in trans-decalin. Recent work consisted of experiments in which proton spin diffusion was used to determine whether cyclooctane was in the lattice of the ordered iPS regions, i.e. in the CVI crystalline regions. These regions have nearly extended (all-trans) chain conformations, based on the x-ray evidence. The high mobility of the cyclooctane molecules (on the microsecond timescale), which is observed in the proton NMR spectra, raises reasonable doubts as to whether a substantial portion of the cyclooctane molecules exist in an ordered polymer region. The result of the spin diffusion experiments, on the other hand confirm that some of the cyclooctane molecules are in the ordered iPS structures.

Morphological Investigation of a Blend of a Rigid Rod Polymer and an Amorphous Nylon

The morphology of a molecular composite composed of polybenzobisthiazole (PBZT) and an amorphous nylon (Zytel 233 from duPont) and prepared by Charles Lee of the Air Force was investigated. The preparation was not the usual coagulation in water from a dilute acid solution. Rather, this sample was initially transformed into a gel in the acid solution and was then solvent exchanged with water, dried, and pressed. Proton spin diffusion measurements, obtained either directly through the proton lineshapes or through ^{13}C CP, were used to obtain morphological information. The spin diffusion results indicated that some of the nylon and the PBZT was intimately mixed in domains where minimum domain dimensions were approximately 4 nm. The mixing was incomplete, however since over dimensions of about 10 nm, the sample-average stoichiometry was not found. In terms of the spin diffusion experiments, an ambiguity remained since the experiments were consistent with a number of models including the extreme cases where some of the nylon was sequestered (greater than 10 nm away) from the PBZT domains, or some of the PBZT was sequestered from the nylon domains. This ambiguity was partially resolved by using proton $T_{1\rho}$ measurements which showed that the PBZT was not sequestered from the nylon.

The spin diffusion studies of this system illustrate two points which have general validity: first, $T_{1\rho}$ measurements can be used to reduce ambiguity in the interpretation of data showing incomplete spin equilibration and second, it is possible to perform these experiments meaningfully when one of the polymers contains only aromatic protons and the other contains a mixture of aromatic and aliphatic protons (the amorphous character of the nylon is achieved by incorporating a significant amount of aromatic monomer).

Off Resonance Proton Irradiation: Influence on Resolution in CP-MAS ^{13}C Spectra and a Method for Separating Methylene and Methine Resonances

In the 1988 Annual Report the application of off-resonance proton irradiation (ORPI) as a method for distinguishing methylene and methine resonances was described. Based on that work, it was clear that ORPI was a good method for distinguishing between these two kinds of resonances when lines were sharp and resonances were distinct. Current work focussed on the use of this method for the more difficult case where resonances of both kinds overlapped. Thus, many more experiments were conducted. As a result of these additional experiments, it has been determined that the separation of methylene and methine resonances in the case of strong overlap is semi-quantitative at best. However, two points emerged which are related to the question of ultimate resolution in CP-MAS spectra. The points are a) the homogeneous contribution to linebroadening in CP-MAS spectra, using **on-resonance** irradiation, depends significantly on the static magnetic field strength and the radio frequency field strength, and b) the homogeneous linewidth contribution due to ORPI is also sensitive to the frequency of the MAS. Both of the above points have not been recognized to date in the literature and both points have important ramifications in terms of achieving the highest possible resolution in crystalline solids, particularly in view of the tendency to perform experiments at higher static fields.

Investigation of Spontaneous Structuring in Asphalt Cements

The Strategic Highway Research Program (SHRP) funded an NMR investigation of asphalt cements in FY89. The objective was to investigate the thesis that asphalts possess domains of differing chemical composition, which composition differs in the concentration of aromatic residues. Six asphalt cements were studied; these asphalts were chosen in the SHRP program so characterization work of various kinds would be performed on the same asphalts.

The work consisted of several experiments. A major effort in assembling experimental apparatus went into aging experiments whose premise was that structuring would exhibit itself as a reduction in the average molecular mobility of the molecules in the asphalt cements. Therefore, proton lineshape changes are expected as this structuring occurred since proton lineshape changes are primarily sensitive to the reorientation mobility of molecules on a microsecond timescale. No significant lineshape changes were observed as a function of any thermal history.

A second set of proton experiments was aimed at obtaining information about the domain size characterizing those molecules (or molecular fragments) whose protons possess the highest molecular mobility. Proton spin diffusion measurements, based on the production of mobility-biased proton polarization gradients, showed that regions of highest mobility were uniformly dispersed throughout the asphalt cement matrix, and that these regions of higher mobility had minimum domain dimensions whose upper limit was 4 - 5 nm. Such a notion is somewhat surprising in view of the proposed micellar model of asphalt cements. If such a micellar model is correct and if the dimensions of the micelles are much larger than 5 nm, then these proton lineshape results suggest that the mobility of the primarily-aliphatic protons in each of these domains is comparable. In other words, the chemical separation implicit in micelle formation is not accompanied by a gradient in mobility.

In a third set of experiments, proton lineshapes were monitored as a function of temperature. The results of these experiments showed that molecular mobility in the typical asphalt cement passed through the microsecond timescale over a temperature range of about 100°C, i.e. the mobility of the individual molecules (or molecular fragments) varied widely. These studies also isolated one of the cements as being unique in the sense that local molecular mobility was more restricted, relative to the other asphalts, at any given temperature. Yet, this cement did not display the highest viscosity. So the relationship between mobility as judged by the proton lineshape and by the viscosity measurements was not necessarily correlated. These experiments also provided perspective for other NMR techniques which could be employed to characterize the asphalt structure. In particular, it is desirable to measure the aliphatic/aromatic ratios and probe whether this ratio varied in different regions of the same asphalt cement. ^{13}C CP NMR was the only way this could be done, and, based on the variable temperature findings, it became clear that the only way ^{13}C spectra could be quantitative was to operate at temperatures where the asphalt approached rigidity on the microsecond timescale, i.e. temperatures of 200°K and below.

In a final set of experiments, proton spin diffusion studies were conducted at 200°K using ^{13}C CP techniques to monitor the aliphatic/aromatic compositional ratios in each of these experiments. The idea was to produce proton polarization gradients between domains, to watch these gradients decay as a result of spin diffusion, and to infer minimum domain dimensions based on the time required for equilibration of the polarization. These experiments were conducted on only two cements, but the results are intriguing. Attempts were made to establish proton polarization gradients based on linewidths, differences in $T_{1\rho}$, and differences in T_1. The former two experiments indicated compositional variations on distance scale smaller than 3 nm. Only the latter experiment gave evidence for differences in aliphatic/aromatic carbon ratio over dimensions larger than 10 nm. In fact, of the two samples looked at, one showed this effect and the other did not. This single observation is the first support for regions of compositional variation larger than 10 nm (as would be expected if micellar structure were present in asphalts) in any of the asphalts.

The Morphology of Crystallizable Polymers

Our investigations have been mainly focussed on poly(phenylene sulfide) [PPS] crystallized from the molten state. This polymer, whose melting point is circa 300°C, is used as the matrix in polymer/carbon-fiber composites for high temperature applications. The development of crystallization in both neat polymer as well as in polymer containing carbon fibers was examined using a phase contrast light microscope equipped with a hot stage and a video-camera. The observations derived from this study bear on two aspects of the crystallization PPS, namely: (1) The nature of the transient stages of the morphological evolution of spherulitic structures from crystal precursors; (2) the nucleating effects of carbon fibers on the crystallization of PPS which is presented in the polymer composites portion of this report.

Mature (i.e. fully developed) polymer spherulites consist of a spherically symmetrical radiating array of chain-folded lamellar structural units. It is common experience however that the spherulites do not evolve in a spherically symmetrical fashion from inception. They usually develop progressively from lamellar crystal precursors (whose lateral growth habits reflect the crystal symmetry of the polymer unit cell), through transient stages of evolution, variously referred to as axialitic or hedritic, in which the proliferation of lamellae is characterized by the profuse manifestation of interlamellar splaying. The causes of the splaying and the origins of the variations in its manifestation among polymers remain speculative. The primary objective of the present study was to determine, at the level of resolution of light microscopy, the general characteristics of the occurrence of interlamellar splaying during the early stages of the evolution of PPS spherulites. This investigation is part of a broader study (involving both light and electron microscopy) whose purpose is to differentiate among the details of spherulite development between those features which are common among polymers, and those which are specific to individual polymers. Such information should provide a more rigorous basis for testing, and developing further, existing phenomenological theories and views on the formation of polymer spherulites.

The temperature of maximum radial growth rate of PPS spherulites grown from the molten state has been reported to occur at about 180°C. Above that temperature the growth rate decreases with increasing crystallization temperature T_c, and nucleation dominates the rate of lamellar growth in the outward (radial) direction. The development of spherulites was examined in films which were 25-50 micrometers thick at T_c in the range 265°C-282°C. A schematic rendition depicting the characteristic <u>outlines</u> (in two different perspectives) exhibited by the precursor structures which develop during the early stages of growth of spherulites at these temperatures is shown in Fig. 1. Using the Cartesian axes XYZ as a frame of reference, Fig. 1a and Fig. 1b illustrate the characteristic appearances of the objects in projection along the Z and Y axes respectively. In marked contrast with the needle-like or acicular profile exhibited by these structures when viewed along Z (Fig.1a), their appearance is distinctly sheaf-like and highly constricted at the center when viewed along Y (Fig.1b). It is evident that the branching and/or interlamellar splaying which underlies the spacial proliferation of lamellae during the development of these precursor structures is highly specific and is predominantly confined to the XZ plane (Fig.1b). Electron microscopic studies of these structures, as well as complementary studies of the crystallization habits exhibited by PPS when crystallized from both dilute and concentrated solutions are planned in an effort to elucidate the fine structural details and the origins of the mode of development of the precursors described above. Meanwhile, some reasonable speculations may be advanced concerning aspects of their morphology.

The unit cell of PPS is orthorhombic. Lamellar crystals grown from dilute solutions are long and narrow with preferential growth parallel to the <u>b</u>-axis [5,6], which is also the preferred radial orientation, and hence the preferred direction of growth of the constituent lamellae in melt-grown spherulites. Accordingly, concerning the early stages of PPS spherulite development depicted above, it may be reasonably concluded that: (i) at the center of the precursor the <u>a</u>, <u>b</u>, and <u>c</u> crystallographic axes in the lamellae are oriented parallel to Y, X, and Z respectively; (ii) the <u>a</u>-axis orientation remains preferentially parallel to Y throughout the structure; (iii) the needle-like habit exhibited by the precursor in the perspective shown in Fig.1a reflects the preferential growth of lamellae parallel to the b-axis, coupled however with interlamellar splaying and or branching 'hinged' about the a-axis direction. These assignments remain to be confirmed as a first step in attempting to elucidate the growth mechanisms which govern the specific characteristics of the development of these precursors.

MEASUREMENT AND MODELING OF MECHANICAL PROPERTIES AND PERFORMANCE

J. C. Crissman, R. S. Duran, K. M. Flynn, C. M. Jackson, G. B. McKenna, L. J. Zapas, and Yihong Chen[1]

The Free Energy Function of Crosslinked Rubbers

The mechanical response and the swelling response in crosslinked polymer networks has generally been treated within the context of the Frenkel-Flory-Rehner (FFR) hypothesis, i.e., the free energy of mixing plus the elastic free energy of the swollen rubber balance in swelling equilibrium. This is generally written as:

$$-RT\,[\ln(1-v_2)+v_2+\chi\, v_2^2] = \frac{V_1}{\lambda^2}\,\frac{\partial \Delta A}{\partial \lambda} \tag{1}$$

where R is the gas constant, T the absolute temperature, v_2 the volume fraction of rubber in the swollen state. χ is the Flory-Huggins interaction parameter, V_1 is the molar volume of the solvent, λ is the stretch and is equal to $v_2^{-1/3}$, and ΔA is the elastic free energy per unit volume of dry rubber.

Importantly, in recent years the validity of equation 1 for crosslinked rubbers has been questioned, yet the evidence has generally been based upon methods which depend on the model used for ΔA or other assumptions, such as χ being independent of crosslink density. In the present work it has been shown that if the FFR hypothesis is valid then a universal relation results between the effective Flory-Huggins interaction parameter and the crosslink density of the network. This result has no model dependence for the elastic energy of the network and depends only upon representing the free energy of mixing as the Flory-Huggins equation suggests. The dependence of χ_{eff} on crosslink density can be expressed as:

$$\frac{\chi_{eff} - \chi_0}{\chi_0} = \alpha \, \nu \tag{2}$$

where χ_0 depends upon the swelling solvent and α appears to be a constant which is independent of solvent. υ is the crosslink density.

The experiments carried out in this study include mechanical and swelling tests on natural rubbers crosslinked with dicumyl peroxide at 1.0 to 20 parts per hundred peroxide. Torsion experiments were carried out in which the torque and normal force were measured as functions of time and deformation. From these results the value of $\partial \Delta A / \partial \lambda$ in equation 1 was calculated. Swelling has been carried out for each of the crosslink density rubbers in a series of six solvents including good, poor and non-solvent systems. The swelling results were used in the calculation of the mixing free energy term in equation 1.

A major assumption in the work described above is that the elastic free energy of the rubber in the swollen state is described by the same function as that which describes the dry state properties. If this is true, then the stress response in the swollen rubber to a mechanical stretch α becomes:

$$\sigma_{11} - \sigma_{22} = v_2 \, \lambda_s [\, \alpha \, w'(\alpha \, \lambda_s) - \alpha^{-1/2} \, \lambda_s \, w'(\alpha^{-1/2} \, \lambda_s)] \tag{3}$$

where v_2 is the volume fraction of rubber and $w'(\lambda) = \partial \Delta A / \partial \lambda$.

Compression measurements on rubber networks swollen to equilibrium were carried out and the results compared with the calculations based on equation (3) and the values of $w'(\lambda)$ determined from the torque and normal force measurements on the dry rubber. The comparisons showed that equation (3) was a valid descriptor of the swollen state behavior for the series of solvents studied. The conclusion was reached, therefore, that the elastic contribution to the free energy of the network was unchanged by the presence of solvent molecules except by the stretch induced in the network. This important result supported one of the major premises of the Frenkel-Flory-Rehner hypothesis.

In future work, the effects of degree of swelling on the tensile response of the rubber will be studied and the swelling activity parameter will be examined simultaneously to further understand apparent deviations from the Frenkel-Flory-Rehner hypothesis and to understand, to some measure, the contribution of the logarithmic term in the free energy function which could not be addressed previously. In addition, experiments to examine the possibility that equation 2 is a universal function in terms of some critical crosslink density, υ^*, are being designed.

Dilatometry of Polymeric Glasses Subjected to Torsional Deformations

There are several important problems in the behavior of glasses which can be addressed by measurements of the volume change in torsion. First, glasses are compressible materials and the strain potential function derivatives with respect to the three invariants of the deformation tensor can be determined by simultaneous measurement of the volume change, torque and normal force response as functions of the angle of twist. Second, the effects of mechanical deformations on the thermodynamic state of glassy materials is currently a subject of considerable controversy, e.g., it is observed that the effects of volume recovery on the mechanical response after a quench from above the glass transition to below it are different in the linear and nonlinear viscoelastic regimes. This "rejuvenation" is not understood and has been variously interpreted by different groups. Measurements of the volume change accompanying aging in samples subjected to torsional deformations of different magnitudes will supply information to better understand "rejuvenation". Third, the free volume and configurational entropy models of the glass transition temperature make different predictions for the effects of a torsional deformation on the glass transition. Dilatometric measurements of the V-T behavior of a network glass subject to torsional deformations should show how T_g behaves as a function of deformation.

A torsional dilatometer was constructed for the purpose of addressing each of the above problems. The device, as designed, has the capability of applying a torque of up to 500 in-lb to a sample up to 6 inches in length. The volume change is measured by floating an LVDT on a 5mm diameter capillary connected to a mercury reservoir surrounding the sample. Machine stiffness, temperature stability of 0.015 K, and micron resolution of the LVDT permit measurements of relative volume changes of 10^{-5} to be measured to an accuracy of better than 1%.

Experiments were carried out on an epoxy network glass which had been aged into equilibrium at several different temperatures from 28°C to 42°C. Torque, Normal Force, and volume change have been measured for deformations from less than 0.01 to 0.15. Preliminary analysis of these data show that the volume change follows a dependence on deformation which is intermediate between a first power and a second power. The interesting finding, at this point, is that the volume change due to the torsion is dilatational for the epoxy studied which is contrary to results reported for other polymeric glasses studied far from equilibrium. The time dependence of the volume relaxation after a single step in deformation is different from that of either the torque or the normal force.

Preliminary experiments have also been carried out to examine the response to a mechanical deformation of the freshly quenched and non-equilibrium glass as it ages towards equilibrium. These results are in the process of being analyzed.

Classical Dilatometry

A set of classical dilatometers is being constructed to complement the torsional dilatometer and to broaden the range of fundamental volumetric studies which this laboratory has the capability of undertaking. Of particular significance, is that the new classical dilatometers will be automated, thus taking much of the labor intensive aspect out of classical dilatometry. In addition, by using the same approach of floating an LVDT on the surface of a mercury meniscus as used in the torsional dilatometer, the sensitivity of the measurement over conventional techniques will be increased by up to a factor of five.

Although construction of the classical dilatometers is only partially completed, several experiments on the epoxy network used in the torsional dilatometer and in concurrent mechanical aging studies have been performed. In addition, preliminary work to characterize the volume-temperature(V-T) response of a 50%/50% blend of polystyrene and poly(vinyl methyl ether) has been done which will complement studies on the phase behavior of these systems carried out in this laboratory by R. Briber and B. Bauer using scattering techniques.

In the future, work will be continued to improve the response of the classical dilatometer systems, continue the characterization of the epoxy network glasses, and attempt to establish the V-T response of blend systems across the entire range of compositions already studied by the scattering techniques. Of particular interest at this time is the fact that preliminary experiments indicate that there is no volume discontinuity at the phase separation temperature. The implications of this result will be explored.

Physical Gelation in Isotactic Polystyrene

In prior work it was postulated, based on NMR studies of solvent molecule mobility, that the apparent solvation of isotactic polystyrene(IPS)/cis- or trans-decalin gels is consistent with a small crystallite size in the solvent which leads to a melting point depression. The DSC measurements which had been performed suggested a reduced heat of fusion of the solvent in the gels due to formation of a polymer/solvent complex. While the measurements by NMR and those by DSC are consistent, the interpretations which have been made are in opposition. Therefore, experiments were tried to determine directly whether or not the solvent crystal size is reduced in a gel and whether or not the magnitude of the reduction is sufficient to explain the observed results. In order to do this, a series of experiments using wide angle x-ray diffraction techniques examines line broadening effects which occur due to small crystallite size in the solvent. In order to do this the current x-ray goniometer was modified to permit experimentation at temperatures from approximately 100 K to 296 K above the normal freezing point of decalin. (The NMR results suggested that the melting point depression may be as much as 150 K in parts of gels from IPS and cis-decalin).

Preliminary results show definite line broadening in a 25% IPS/cis-decalin gel. The results appear to be richer than simply finding a reduction in crystallite size as effects, such as no broadening of certain peaks, while others show significant broadening, suggest a significant amount of crystallite anisotropy of form. These effects remain to be verified and explored more deeply.

In addition to the above study, this work has branched in two ways which are important from a fundamental point of view. First, in the x-ray diffraction catalogs available at NIST the crystal structures of cis- and trans-decalin could not be found, perhaps because of the low (≈-30°C) melting point of decalin. A literature search also revealed no crystal structure for these low molecular weight compounds. If the structure cannot be found, our reports will include preliminary structural data on cis and trans decalin. The second branch is directly related to the problem of melting of small crystallites. A standard pore size material is sought to understand what may be happening in the IPS gels if indeed the crystal size has been reduced. Therefore, the effects of pore size on the melting point of various solvents using Vycor glass, controlled pore glasses and aerogels were studied to examine the effect of pore size on melting behavior. It also suggests a method for the determination of the liquid/solid interfacial energy by combining x-ray and DSC measurements on these systems. These latter experiments are currently only exploratory.

Rubber Standard Reference Materials

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 NBS 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 NBS 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, work has been proceeding to procure and recertify the SRM 386I (Styrene Butadiene Rubber) thus renewing the stock of this material.

Multistep Stress-Relaxation Study of a Single Crystal of n-Eicosane ($C_{20}H_{42}$) In Torsion

The multistep stress-relaxation behavior in torsion of a single crystal of the long chain hydrocarbon compound n-eicosane has been examined in the region of relatively small deformations. It is found that when the strain in torsion is less than about 6×10^{-4} the behavior very nearly approaches that of a linear viscoelastic solid in which the time dependence of the relaxation modulus is only very weak. At larger strains the behavior becomes increasingly nonlinear and time dependent. The multistep stress-relaxation response has been analyzed in terms of two constitutive relations, one the BKZ theory developed by Bernstein, Kearsley, and Zapas, and the other a recent formulation proposed by Zapas. In the region of strain where the stress-strain behavior becomes highly nonlinear the experimental results can be described quite well by using the recent treatment given by Zapas.

According to the BKZ theory, the stress $\sigma(t)$ at any time t during a stress-relaxation experiment is given by

$$\sigma(t) = -\int_{-\infty}^{t} W_*\left(\frac{\lambda(t)}{\lambda(\tau)} - 1, t-\tau\right) d\tau \tag{1}$$

where $\lambda(t)$ and $\lambda(\tau)$ are the principal extension ratios at times t and τ respectively, and $\tau<t$. $W_*(\bullet, \bullet)$denotes the derivative of $W(\bullet, \bullet)$ with respect to the second argument and $W(\bullet, \bullet)$ represents a strain energy density. For a single step stress-relaxation history $\sigma(t) = W(\lambda,t)$, where $W(\lambda,t)$ is the stress relaxation function at stretch λ and time t. In principle, one can from a knowledge of the single step stress-relaxation behavior predict the behavior for any other deformation history involving the same type of deformation. In the event that the deformations are small, equation (1) can be rewritten in the form

$$\sigma(\tau) = -\int_{-\infty}^{t} W_*(\gamma(t) - \gamma(\tau), t-\tau)\, d\tau \tag{2}$$

where $\gamma(t)$ and $\gamma(\tau)$ represent the strain in torsion at times t and τ respectively, and $\sigma(t)$ is the shear stress.

For an experiment in which the magnitude of the second step is one half the value of the first step integration of equation (2) gives the following relation

$$\sigma(\gamma_1, t) = 2W(\gamma_1/2, t) - W(\gamma_1/2, t-t_1) \tag{3}$$

Evaluation of equation (3) requires a knowledge of the single step stress-relaxation behavior at one half the value of the strain during the first step.

More recently, Zapas has suggested a new constitutive equation which includes an additional term yielding

$$\sigma(t) = -\int_{-\infty}^{t} W_{\bullet}(\gamma(t)-\gamma(\tau), t-\tau)\,d\tau +$$
$$+\left\{\int_{-\infty}^{t} F_{\bullet}(\gamma(t)-\gamma(\tau), t-\tau)\right\} \tag{4}$$
$$\left\{\int_{\tau}^{t} - \int_{-\infty}^{\zeta} \phi_{\bullet\bullet}(\gamma(\zeta)-\gamma(\theta), \zeta-\theta)\,d\theta\,d\zeta\right\} d\tau$$

where $F(\bullet,\bullet)$ and $\phi(\bullet,\bullet)$ are functions which are properties of the material.
Here $\phi_{\bullet\bullet}(\bullet,\bullet)$ denotes the second derivative of the function $\phi(\gamma,t)$ with respect to the second argument. For a single step stress-relaxation experiment
equation (4) becomes

$$\sigma(\gamma,t) = W(\gamma,t) - F(\gamma,t)\,\theta(\gamma,t) \tag{5}$$

The functions $W(\gamma,t)$ and $F(\gamma,t)$ are odd functions in γ, whereas $\phi(\gamma,t)$ is an even function in γ. In this description a knowledge of the single step stress-relaxation behavior is not sufficient to describe other strain histories of the same type. Additional information is required which only can be obtained from a series of multistep stress-relaxation experiments.

For the same two step experiment in which the magnitude of the second step strain is one half that of the first step, the following expression is obtained from equation (4)

$$\sigma(t) = (BKZ) + (F(\gamma,t-t_1) - F(\gamma,t))\,\theta(2\gamma,t) -$$
$$-F(\gamma,t)\{\theta(2\gamma,t_1) - 2\theta(\gamma,t) - \theta(\gamma,t-t_1)\} - \tag{6}$$
$$-\int_{t-t_1}^{t} F_{\bullet}(\gamma,\zeta)\,\theta(2\gamma,t-\zeta)\,d\zeta$$

where by (BKZ) is meant the prediction given by the BKZ theory for this particular strain history within the context of the new formulation.

A series of two step stress-relaxation experiments was done in which the strain, γ, during the first step was varied from $5.6\text{x}10^{-5}$ to $7.5\text{x}10^{-3}$. An example of the second step response is shown in Figure 1 for the case when γ, was $7.5\text{x}10^{-3}$ and the behavior was highly nonlinear. The triangles correspond to data obtained from a single step experiment in which the magnitude of the strain was $3.75\text{x}10^{-3}$ and the filled circles to the data obtained from the second step of the two step experiment in which $\gamma_1 = 7.5\text{x}10^{-3}$. The circles with a cross represent the second step response predicted by the BKZ theory and the filled squares the second step response calculated using the formulation by Zapas. It was found possible to fit all of the second step data very well from each of the experiments using equation (6), where the function F(γ,t) and ϕ(γ,t) are given by

$$F(\gamma,t) - 7.0x10^3\,\gamma^{0.55}t^{-0.16} \qquad (7)$$
$$\phi(\gamma,t) - \gamma^{1.0}\,t^{0.013}$$

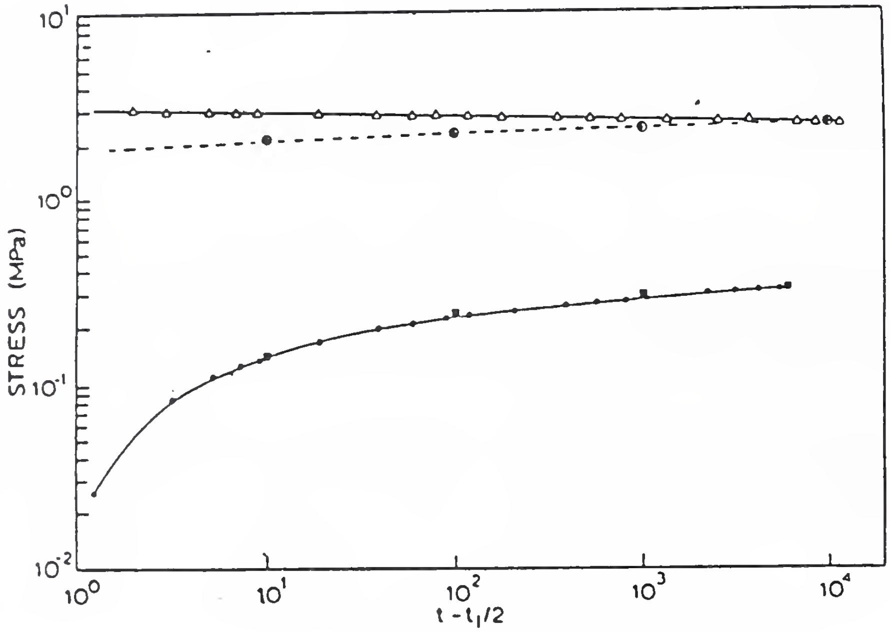

Figure 1 Log stress versus log $(t-t_1/2)$ for an experiment in which $\gamma_1 = 7.50x10^{-2}$ and $\gamma_2 = 3.75x10^{-3}$. △ - $\gamma_1 = 3.75x10^{-3}$, • - $\gamma_2 = 3.75x10^{-3}$, ⊕ - response predicted by the BKZ theory, ☐ - second step response calculated using equation (6).

Physical and Chemical Aging of PMMA and Their Effects on Creep and Creep Rupture Behavior

In previous work it was found that the failure behavior of poly (methylmethacrylate)[PMMA] in uniaxial creep could be successfully described using a failure criterion in which the time to failure multiplied by the strain rate at failure is constant, i.e., $t_f\ \dot{\varepsilon}_f$ = constant. A set of relationships was also derived which established a linkage between the viscoelastic behavior of the PMMA and the success of the failure criterion; viz., the creep retardation spectrum did not change with applied stress (time-stress superposition was valid), the vertical shift b_σ required to superimpose the creep compliance curves at different stress levels was equal to the ratio of the stress for the curve of interest to that of the reference curve ($b_\sigma = \sigma / \sigma_{ref}$), and the strain at failure was constant and independent of the level of the stress. It was also found that the same <u>failure constant</u> ($t_f \ \varepsilon_f$) described both the behavior of a freshly quenched (to room temperature) PMMA and one which had been aged for approximately 5 years at room temperature, i.e., as received. The creep curves obtained at different aging times for both sets of samples tested at room temperature could also be superimposed, thus, showing consistency of the behavior of the PMMA studied with the <u>time-aging time correspondence</u> principle.

The study of the validity of the failure criterion and the time-aging time-stress superposition principle for PMMA glasses has been extended by considering glasses which have been aged at 80°C for up to 254 days after a quench from above T_g to 80°C and subsequently tested at room temperature. It is found that the behavior of the PMMA follows the same rules as described above. However, the creep responses of the samples studied here (i.e., aged at 80°C and tested at 22.5°C) cannot be superimposed upon those obtained previously which were aged and tested at 22.5°C. For a given aging time the creep curves are superimposable and the strain at failure is approximately constant and independent of the stress. The same failure criterion found previously is therefore valid for the test conditions described here. For aging times of up to 11 days the strain failure is found to be constant and independent of the aging time. The decrease in strain at failure is accompanied by a decrease in the molecular weight of the polymer as a result of chemical degradation during the physical aging process.

As was found previously, the stress dependence of the viscoelastic shift factor a_σ is the same as that of the failure time. However, once the strain at failure changes, the failure times are no longer related to the aging time shift factor a_{te} alone.

Multistep Stress-Relaxation Behavior in Uniaxial Extension of an Ethylene-Hexene Copolymer

The theory of viscoelastic fluids proposed by Bernstein, Kearsley and Zapas has been found to give a reasonable description of the mechanical behavior of melts and concentrated polymer solutions. However, it is known for certain classes of motions, quantitative agreement with experiments cannot be obtained. This led Zapas to propose a three dimensional constitutive equation which adds to the term given by the BKZ theory a cross term represented by a triple integral. This additional term comes about as a correction which results from the dependence of the material clock on the previous strain history. Recently a phenomenological theory has been presented by Coleman and Zapas for the class of viscoelastic fluids for which internal structural changes occur at a rate that is influenced by the strain history (including volume changes). They, as in the case of the BKZ theory, consider the class of simple fluids broad enough to include materials which have an infinite viscosity. Under this condition, the aforementioned theories should describe the non-linear behavior of semicrystalline polymers at reasonably small deformations (deformations before necking occurs) and for strain histories where the BKZ theory does not give quantitative agreement with the experiments. In order to determine the functions involved in the cross term which appears in the new description, one needs not only the behavior of the single step stress relaxation response but also a set of multistep stress-relaxation data at various strains and times. Having determined these functions one can calculate any other multistep history and compare the predictions with experiments.

As in the BKZ theory, the general equations given by the new description may be specialized to one dimension, where it is assumed the effects due to volume changes are included in the second term. This leads to the following equation

$$\begin{aligned}\sigma(t) = &-\int_{-\infty}^{t} H_{*}(\varepsilon(t)-\varepsilon(\tau), t-\tau)\, d\tau + \\ &+ \left\{\int_{-\infty}^{t} F_{*}(\varepsilon(t)-\varepsilon(\tau), t-\tau)\right\} \\ &\left\{\int_{\tau}^{t} - \int_{-\infty}^{\xi} \phi_{**}(\varepsilon(\xi)-\varepsilon(\theta), \xi-\theta)\, d\theta\, d\xi\right\} d\tau\end{aligned} \tag{1}$$

where the star is used to denote the derivative of a function with respect to its second argument. By $\phi_{**}(\cdot,\cdot)$ is meant the second partial derivative of the function $\phi(\varepsilon,t)$ with respect to the second argument. In this formulation the stress from a single step stress-relaxation experiment is given by the following expression

$$\hat{\sigma}(\varepsilon,t) = H(\varepsilon,t) - F(\varepsilon,t)\,\phi(\varepsilon,t) \tag{2}$$

The functions $H(\varepsilon,t)$ and $F(\varepsilon,t)$ are odd functions in ε while $\phi(\varepsilon,t)$ is an even function, and $H(\varepsilon,\infty)$, $F(\varepsilon,\infty)$, and $\phi_{*}(\varepsilon,\infty)$ are zero. It is evident that in this description, unlike for the BKZ theory, a knowledge of the single step stress-relaxation behavior surface is not sufficient to predict other strain behavior. One needs in this case more information which can be obtained from a series of multistep stress-relaxation experiments. The presence of the cross product in the last term of equation (1) complicates the entire procedure and one no longer has the simplicity of the BKZ theory.

As an example of the application of the new description results from two step stress-relaxation experiments done on an ethylene-hexene copolymer in which the second step in strain was half the value of the first were analyzed. From equation (1)

$$\begin{aligned}\sigma(t) = (BKZ) + (F(\epsilon, t-t_1) - F(\epsilon,t))\,\phi(2\epsilon,t_1) - \\ -F(\epsilon,t)\{\phi(2\epsilon,t_1) - 2(\phi(\epsilon,t) - \phi(\epsilon,t-t_1))\} \\ -\int_{t-t_1}^{t} F_{*}(\epsilon,\zeta)\,\phi(2\epsilon,t-\zeta)\,d\zeta\end{aligned} \qquad (3)$$

whereby (BKZ) here denotes the prediction given by the BKZ theory for that particular strain history within the content of the new description.

Shown in Figure 1 are second step data from experiments involving a strain history in which $\varepsilon_1 = 0.020$ and $\varepsilon_2 = 0.010$. The triangles correspond to the actual data for the case when $t_1 = 6.4$ seconds and the circles to the case when $t_1 = 819.2$ seconds. The dashed lines represent the predictions of the BKZ theory and the filled circles to the values calculated using the new description. The left hand branch of both set of predictions represent negative values. It can be seen that the predictions of the new description are in very good agreement with the actual data, whereas the predictions of the BKZ theory fall well above them.

The new description was also successfully used to fit the data from an experiment in which the strain was increased at a constant rate to a strain of two percent and then decrease at the same constant rate back to zero stress. The addition of the cross term in the new formulation appears to provide the necessary ingredient in order to describe quantitatively the behavior observed in experiments involving rather complex strain histories.

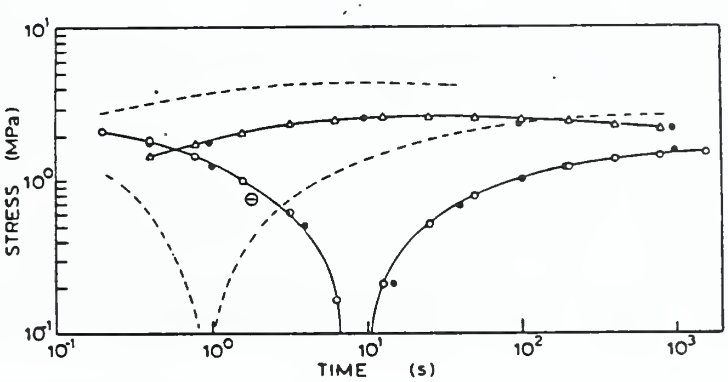

Figure 1 Second step stress-relaxation data from an experiment involving the strain history described by case (b), where $\varepsilon_1 = 0.020$ and $\varepsilon_2 = 0.010$. The solid lines correspond to the actual data, the dashed lines to the predictions of the BKZ theory, and the filled circles to the predictions of the new derivation. Triangles - $t_1 = 6.4$ seconds, open circles - $t_1 = 819.2$ seconds. ⊖ denotes negative values.

POLYMER COMPOSITES

One of the most rapidly growing areas in the materials field is polymer based composites. Their high specific strength and stiffness combined with their versatility in the manufacture of complex parts give them tremendous potential for applications ranging from transportation to construction. For advanced composites, growth rates of 16 percent per year and higher are frequently cited. To maintain this growth rate, however, it will be necessary to overcome major problems in two areas. First, there is a need to make processing more rapid and reliable. Second, improvements must be made in our ability to understand and predict performance, particularly long term durability.

To achieve these goals, the underlying science base, which is currently rather weak, must be significantly strengthened. This is particularly critical now since composites are moving beyond aerospace and DOD applications into commercial areas such as automobiles, electronics, and construction. Advances in these areas are critical to the international competitiveness of U.S. industry. In response to this opportunity, the effort on polymer composites has undergoing a major expansion facilitated by the Initiative on High Performance Composites which began in 1988.

The program is divided into three areas: Processing, Structure, and Performance. The current activity in the Processing area focuses on the development of a composite fabrication facility at NIST. Equipment for autoclave molding, press molding, and resin transfer molding are included. This will permit the preparation of well-characterized test samples and the investigation of processing science and on-line process control. These are the keys to more rapid and reliable processing. In addition to building the fabrication facility, work is continuing on the study of process monitoring techniques, and new programs on process modeling are being developed.

The second area, Structure, seeks to bridge the gap between processing and performance by developing techniques to characterize the microstructure of composites systems. Research during the past year has continued the studies of molecular structure in thermoset polymers and in gel-spun fibers and films, has expanded the program investigating crystallinity in thermoplastics, and has added two new projects. The first new project is surveying the techniques with potential to characterize the microstructure and properties of thick section composites. The second focuses on the fiber-matrix interface. This latter program has just begun, and so no results are yet available, but it will be developing new test methods and evaluating current methods for interface bond strength.

The Performance area involves the determination of properties for composites and their constituents. During the past year, the research has focused on the characterization of resin failure behavior, the development of test methods to characterize interlaminar fracture of composites, the modeling of failure in compression, and the evaluation of composites data bases for the future.

To assist in these efforts, the Polymer Composites Group has utilized cooperative programs and guest experts. The cooperative programs have included projects with the Departments of Defense and State, and the industrial research laboratories of duPont, Ferro, Hi-Tek Polymers, and Polaroid. Interactions with two industry groups, the National Center for Manufacturing Science and the Suppliers of Advanced Composite Materials Association have also contributed significantly to the Groups's programs. Joint programs with universities have involved Johns Hopkins, University of Massachusetts, and Michigan State University. In addition, Prof. Hiroshi Mizumachi from the University of Tokyo is working at NIST in the Polymer Composites Group studying fracture behavior of toughened resins. The Colloquium Series on Composite Materials has continued to bring many world renown scientists to NIST for discussions. Finally, Herzl Chai, Fred Phelan, and Walter McDonough have joined the staff at NIST during the past year, and will greatly increase the research effort on composites.

FY 89 Significant Accomplishments

- To describe resin transfer molding, a new model was developed for the flow of a viscoelastic fluid into a porous medium. The new model fits experimental data for inelastic fluids as well as existing models and, in addition, it successfully predicts the limiting flow behavior when the elastic component of the fluid behavior is large.

- Experiments confirm that molecular segregation can occur during crosslinking for systems where one component is a blend of two different molecular weights. The study here provides unequivocal evidence of the non-random nature of the molecular arrangement in the resulting network. In general, such systems have superior properties, and this result is a critical step in understanding why.

- Infrared dichroism measurements have shown that the response of the molecular networks in epoxies to deformation is predominantly an unfolding mechanism. This is consistent with previous results from small angle neutron scattering measurements. Such results are critical to optimizing the mechanical properties of thermosets and hence their composites.

- A previously developed technique to measure the resistance of polymer resins to interlaminar crack growth in their composites was extended to the shearing fracture modes. The test uses a thin adhesive bond between metal adherends to simulate the constraint on the resin deformation produced in the composite by the fibers. Results show excellent correlations between the shearing fracture energies obtained in the adhesive joint test and the composite measurements.

- A simplified mixed-mode fracture analysis was developed to model delamination in composites and adhesive bonded systems subjected to compressive loads. The analysis identified explicitly the geometric and materials properties of the debonded structure that control crack propagation or arrest, and thus it can be used as a basis for designing composite or adhesively bonded parts against delamination failure.

PROCESSING

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The Processing activity seeks to develop an understanding of the events that occur during processing, to formulate models that describe these events, and to study the implementation of on-line process control. Current work is developing a composite fabrication facility at NIST to assist in this effort. Test methods to monitor processing events are also being developed. Finally, research on modelling has been initiated. Progress to date in each of these areas is discussed below.

Composite Processing Facility

An industry workshop on composite processing held at NIST on October 7, 1987 identified two processing methods as being the most promising fabrication techniques for the future. They were pressure molding and resin transfer molding. Pressure molding via autoclave is an important process in the aerospace industry while pressure molding via hydraulic press dominates in the electronics industry for circuit boards. Resin transfer molding is of particular interest to the automotive industry, but it is also becoming more popular in aerospace and other sectors as well because of its speed and low cost. The workshop also identified scientific and technical barriers that hinder improved processing. The most important barrier was the need for a better scientific understanding of processing, i.e., knowledge of resin and heat flow, factors controlling fiber orientation, morphology changes, interface effects, etc. This understanding was regarded as a critical step in implementing on-line process control.

In response to these conclusions, the Polymer Composites Group is currently remodeling several laboratory modules to accommodate processing equipment of all three types of fabrication: a prepreg machine and autoclave, a hydraulic press, and facilities for resin transfer molding. Each of these has been designed to maximize the opportunities for on-line monitoring and flow visualization so the processing events can be studied to gain a better understanding of the underlying science, and to facilitate the investigation and implementation of on-line process control.

The autoclave will have the capability to operate at high temperatures (538°C) and pressures (3.8 MPa). In addition to extra ports for process monitoring equipment, a video camera will be attached so that events inside the autoclave can be recorded. The prepreg machine permits the preparation of specialized composite samples and has the capability to add specific fiber surface treatments. The hydraulic press will provide a simple geometry for initial studies of process monitoring in the lamination process and will be computerized to facilitate experiments in on-line process control. The resin transfer molding facility will be designed to study the flow of resins into molds containing preforms using techniques such as flow visualization. Special instrumented molds and pumping systems are currently under design.

In addition to the processing equipment, other facilities are being added to increase the capabilities for modeling and characterizing the basic properties of fluids and solids. A linear viscoelastic characterization device for determining the tensile, compression, and bending properties of polymers and polymeric composites has been installed, and a similar device for fluids is being added. This equipment is highly automated and can measure both transient and dynamic mechanical properties over a wide range of temperatures. The information obtained will be used to characterize the materials employed in the processing experiments and as input for process modeling studies.

Finally, a super-computing graphics workstation is being added to perform process modeling and stress analysis tasks. In addition, it will be equipped with a sophisticated image analysis system so that complex flow visualization and other pictorial data can be treated rapidly. The facility will have the ability to capture, store, and analyzed video and other image data.

The schedule for completion of the processing facility is the end of FY90, but many components will be operational early in the year. In preparation for this, work is being pursued to develop process monitoring techniques and the associated science base. The first application will be in the autoclave and press molding facilities with thermoset resins, but tests with thermoplastics will follow. In addition, a program on resin transfer molding is being developed which combines the flow visualization experiments and modeling studies.

Process Monitoring Techniques

An important accomplishment of the past work in the Processing subtask has been the development of a unique capability and expertise in process monitoring techniques. This work has produced or implemented 10 different measurement methods to monitor the events that occur during processing. These techniques permit measurement of mechanical, thermal, electrical, optical, as well as chemical and structural properties. Ultimately, a number of these methods will be implemented on-line in the new processing facility. During the past year, this expertise has been used to address three specific problem areas.

Survey of Process Monitoring Techniques.

In cooperation with industries interested in composite processing, the present state of process monitoring technology was surveyed and the important areas for future development were identified. It was concluded that past development work in the areas of ultrasonics, dielectrics, optical, and spectroscopic methods make them quite promising for process monitoring. The need to continue development of these techniques was emphasized as was the importance of establishing the relationships between the properties measured by these tests and parameters more directly related to processing such as viscosity and degree of cure. Finally, the numerous large programs that are developing process control models and technology were considered, and the value of such programs for the development of on-line process control was noted. These programs, however, do not focus on sensor development and the generation of the science base needed for interpretation of the sensor output. Consequently, the need for increased efforts in these areas was strongly recommended.

Development of Ultrasonic Cure Monitoring.

A second area of activity investigated ultrasonic measurements. This is one of the most popular cure monitoring techniques for polymer composites. The particular method studied in the NIST program utilizes high frequency shear wave propagation to characteristics the high frequency dynamic shear modulus, G^* of the sample. To make this measurement more meaningful for process control, however, G^* must be related to quantities that provide more direct insight into the changes that are critical to processing, for example, viscosity and degree of cure. As a result, a program seeks to correlate the ultrasonic measurements with steady flow viscosity.

A series of experiments were being performed using epoxy (diglycidyl ether of bisphenol A) cured with nadic methyl anhydride and benzldimethylamine. Samples cured at different temperatures were monitored using both ultrasonic and viscosity measurements. The results exhibited an excellent empirical correlation between the two measurements during the early phases of cure where viscosity is an important parameter.

In an effort to establish a basis for this correlation, the relationship between the zero shear rate viscosity, η_o, and the real part of the dynamic shear modulus, G' is being investigated. This relationship is

$$\eta_o = \frac{2}{\pi} \int_{-\infty}^{\infty} \frac{G'}{\omega} \, d \ln \omega$$

where ω is the angular frequency. Simple models are being used to apply this relationship to the cure monitoring data. It is too early to judge the success of this approach in quantitatively relating the two measurements, but it is clear that the study provides new insight into the usefulness of ultrasonics. For example, the results help delineate the range of materials and cure states where the ultrasonic technique provides a sensitive tool to monitor cure. It is hoped that this study will eventually provide a means to quantify such results.

Cure Monitoring with Differential Scanning Calorimetry.

Another valuable tool for studying reactive systems and developing cure cycles is differential scanning calorimetry (DSC). During the past year, this technique was used to examine three important systems: a phenolic cured epoxy, tetra-functional epoxy cured with diaminosulfone (DDS), and polycyanurates formed from dicyanates.

The phenolic cured epoxy is a commercial coating for steel plates. An important problem for this and other similar systems is the need to determine an optimum cure cycle. A detailed DSC study was conducted and a new procedure was developed using both scanning and isothermal curing, as well as post-curing and relaxation near the glass transition temperature to provide the necessary data for cure cycle optimization. This procedure was successfully applied to the phenolic system.

The tetra-functional epoxy cured with DDS is a popular high performance, high temperature resin used in the aerospace industry. Detailed DSC studies revealed some difficulties with tests on this resin at high temperatures. The results suggest that there is some loss of volatiles and perhaps large volume changes or contractions occur during the curing process. As DSC measurements depend strongly on thermal diffusivity, the drastic changes in the thermal contact of the resin with the sample container causing sudden shifts in the baseline and large uncertainties in the magnitude and the direction of the heat flow. Identification of this problem is the first step in developing improved procedures for this important resin system.

Dicyanate monomers and oligomers convert upon heating into thermosetting polymers containing stable cyanurate rings. DSC was used to compare the efficiencies of different catalyst systems and to determine optimum conditions for cure. As the monomers crystallize readily, there is a need to find a means to change the raw resin into a liquid for easier applications. Current work is investigating methods to accomplish this by blending with other liquid resins.

Development of a Transfer Molding Research Program

The third major area of research in Processing is resin transfer molding. Numerous discussions with industrial researchers and a thorough review of the literature has identified the most critical issue to be resin flow during mold filling. Three areas are the keys to addressing resin flow. First, a better understanding of the physics of the process is required, and process modeling is an important tool in this area. Second, carefully chosen experiments are needed to help develop, test, improve, and verify processing models. Finally, new theoretical formulations are required to model the flow of rheologically complex fluids in porous media and the complex rheo-kinetic changes which occur in transfer molding with thermosets. A program plan has been developed to address all three of these areas, and very encouraging preliminary results on the third topic have already been obtained.

In the first area, numerical schemes are being investigated to solve the equations which describe the isothermal flow of a Newtonian fluid in porous media. The computer simulation will later be extended to cover non-isothermal flow with chemical reaction, and mold filling with (particle) filled systems and viscoelastic materials. The initial experimental work is focusing on flow visualization experiments, and to this end a mold is being constructed which will permit such experiments.

In the theoretical area, preliminary results have been obtained using a new relationship which describes the flow of viscoelastic fluids in porous media. This relationship was derived using dimensional analysis and scaling arguments based on the structure of the Cauchy momentum balance and the Giesekus constitutive equation. A plot of flow resistance (given by the quantity fRe; friction factor multiplied by Reynolds number) versus the Deborah number (denoted De; a measure of the importance of fluid elasticity in the flow) shows that the predictions of the model compare well with the literature data of Marshall and Metzner for low to moderate Deborah numbers. Moreover, the model offers some improvement over the only other existing relationship for viscoelastic flow in porous media which was derived by Wissler. In contrast to the Wissler relation, the equation derived here predicts a limiting value of fRe at high Deborah numbers which is in qualitative agreement with existing experimental data of Haas and Durst. Further work to improve the model, and obtain greater quantitative agreement with experiment is now underway. A model which describes the flow of (particle) filled materials in porous media has also been developed, but has not yet been compared with previous results.

STRUCTURE

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The determination of the microstructure of a composites and its matrix resin, the dependence of this structure on processing, and the role of microstructure in determining the material's performance properties are the major thrusts. Four research areas are currently under study. First, a program is investigating the effects of carbon fibers on the crystallinity in partially crystalline thermoplastics. Second, a major effort investigating the network structure in thermoset resins and the response of this structure to deformation is continuing. Third, the formation and properties of fibers and films formed by gel spinning is under study. Finally, a small program has examined the question of characterizing the matrix microstructure in thick section composites.

The Nucleating Effect of Carbon Fibers on the Crystallization of PPS

The morphology, crystallinity, and hence the mechanical properties, of crystallizable thermoplastic polymer matrices used in polymer/fiber composites can vary over a broad range depending on the thermal conditions used in manufacture, as would be the case for neat polymer products. There is however an additional factor which influences the polymer morphology in composites and that is the manifestation of 'transcrystallization' at the polymer fiber interface. Its occurrence results from the simultaneous initiation of spherulites from closely spaced sites (e.g. of the order of a few micrometers from one another) at the fiber surface. Because of the high surface density of the nucleation sites, spherulitic development from individual sites is hindered laterally to such an extent that it is essentially limited to growth in the direction normal to the fiber surface. In short, the manifestation of transcrystallization of the polymer at the polymer fiber/interface is characterized by the formation of an annular sheath of crystallized polymer around individual fibers and extending along their length. The lamellae in this transcrystalline sheath develop preferentially radially outwards at right angles to the fiber surface. The crystallographically preferred orientation characteristics of the lamellae relative to radial paths in the sheath correspond to the radial orientation of lamellae in mature spherulites.

The manifestation of transcrystallization at the surface of carbon fibers in fiber containing polyphenylene sulfide (PPS) samples has been previously reported by Johnson and Ryan, and Wadden and coworkers. The type of carbon fiber was not specified in the former study. In the latter study two types of polyacrylonitrile based carbon fibers (referred to as ex-PAN carbon fibers in the text below) were used namely, high modulus (HM), and high strength (HT) fibers. Of these two types, the HM fibers, which were described as having been surface treated in commercial production, did induce the transcrytallization of the polymer at the surface of the fibers. No transcrystallization was observed in the case of the HT fibers which, however, had an epoxy surface coating. No meaningful comparison between the nucleating properties of the two types of fiber could thus be made.

In order to determine aspects of carbon fiber morphology which influence transcrystallization, an investigation of the nucleating effects of carbon fibers on the crystallization of PPS has been started. Experiments on polymer containing short lengths of fibers cut from continuous filaments have been carried out at crystallization temperatures in the range 265°C-280°C. The effects of three different types of commercially available ex-PAN carbon fibers has been examined so far: a type-HM, a type-HT, and a third type, denoted IM, which is an intermediate modulus fiber. The fibers had no surface coatings (sizing), but all had been "surface treated" in manufacture. The details of the surface treatments used in industrial carbon fiber production are proprietary. They are commonly oxidizing in nature, and their purpose is to enhance adhesion between the polymer matrix and the fibers.

Whereas preferential nucleation resulting in transcrystallization was induced at the surface of the HM fibers, no such effect was manifested in the case of the HT or the IM fibers. Such differences between the effects of HM and HT fibers have been observed with other polymers.

In an effort to further probe the influences, with regard to trans-crystallization, of differences in surface treatments, differences in fiber surface topography, as well as crystallographic, orientational, and morphological differences among carbon fibers, future investigations will include the study of the nucleation effects on PPS, of ex-Pan fibers which have not been subjected to surface treatments. A comparative study of the nucleation effects of commercial pitch-based carbon fibers will also be undertaken.

Network Structure in Thermoset Resins

The molecular architecture of thermoset resins consists of large networks, and the structure of these networks is critical to the properties of the resin. The current studies build on previous

NIST research and explore structure-property relationships. Earlier research with epoxy networks had shown that an unusual structure was generated when the curing agent was a mixture of two different molecular weight amines. To examine the generality of this result, new studies were performed using polydimethylsiloxane networks. A second project is examining the generality of previous results on simple epoxy-amine formulations by testing an epoxy cured without a crosslinking agent and by examining a commercial resin system. Finally, previous work had used small angle neutron scattering to study molecular orientation during deformation. To compliment that study, new research have used optical methods to examine the same systems and compare the results.

Molecular Structure of Bimodal Polymer Network

Crosslinked systems are often modified by adding small amounts of an intermediate molecular weight material which reacts into the molecular network. This can be done by using as one of the reacting materials, a component with a bimodal molecular weight distribution. It would be expected that the different molecular weight molecules are incorporated into the network in a random fashion. Previous work using an epoxy cured with a mixture of two different molecular weight amines, however, found that the molecular structure was not random. This has important implications for structure-property relationships so it is necessary to determine if other systems show similar results.

Literature results are available for a network was prepared from polydimethylsiloxane having a bimodal molecular weight distribution. If the reactions are exclusively at the end of the chains, the chain length distribution in the network will be identical to that of the material before reaction. The networks generated with this bimodal system exhibit some unique features comparing networks made from unimodal starting materials· The most noticeable difference is the ultimate strength before break; the bimodal networks are much stronger or tougher than the unimodal ones. Previous studies have examined stress-strain, stress-birefringence and stress-temperature measurements to elucidate the cause of the superior mechanical properties of bimodal networks· Experiments which provide a direct characterization of the molecular structure in the networks made from starting materials with a bimodal molecular weight distribution, however, have not been carried out. Consequently, a small angle neutron scattering (SANS) study was undertaken on a third system consisting of bimodal polytetrahydrofuran which was selected because the deuterated materials necessary for SANS experiments could be obtained. The question to be addressed is whether the short and the long chains enter randomly into the bimodal network. A random disposition of the long and the short chains within an average network is the obvious choice and was assumed in all the previous work, at least implicitly.

For all the SANS specimens, every short chain is deuterated while the long chains are not. Three different samples were prepared with different bimodal distributions and concentrations of initiator. For each sample, SANS measurements were conducted on the uncured, the completely cured and a few partially cured samples. For the uncured sample (curve a), the scattering intensity at zero scattering angle is estimated to be 0.7cm^{-1} which is very close to the theoretical value of 0.74 for the prepolymer pair assuming ideal mixing. This result strongly suggests that the mixing of the long and the short chains in the uncured state approaches that of an ideal solution.

If crosslinking does not induce either molecular or phase segregation between the hydrogenated long chains and the deuterated short chains, the SANS scattering intensity will not be changed by crosslinking. The experiments, however, show a dramatic increase in intensity in the small q range during the initial stages of cure. This provides unequivocal evidence for segregation. As cure proceeds to completion, however, the scattering intensity, especially in the low q region, exhibits a marked decrease. In addition, a weak maximum in the scattering intensity for the fully cured samples appeared around a q value of 0.04 $Å^{-1}$. This trend was observed in all samples. The weak maximum resembles what is observed for regular block copolymers.

In summary, the SANS results strongly suggest that crosslinking can induce segregation in bimodal network. This result is consistent with the earlier finding with an epoxy-amine system. In light of this new discovery, some of the earlier observations made on bimodal network need to be re-examined.

Characterization of Molecular Network of Epoxies Using Neutron Scattering

Our efforts using neutron scattering to characterize the molecular network in epoxies have been productive over the last few years. The early results with partially deuterated diglycidyl ether of bisphenol A (DGEBA) cured with Jeffamines[*] can be fitted quantitatively with the random phase approximation scheme. The presence of amines, however, adds uncertainty to the interpretation of experimental results. In uncured mixtures the scattering pattern is perturbed by the amines. Moreover, the presence of amines make data interpretation more complicated in the cured system since the proton containing portion of the network includes a combination of the amine and the protonated portion of DGEBA. Although the fit between the calculation and experimental scattering results is quite satisfactory, the question concerning the sensitivity of the results for elucidating the network structure remained.

To answer this question, the following experiment was conducted. The partially deuterated DGEBA (d-DGEBA) was cured without any amines. It is well known that homopolymerization of DGEBA will occur at elevated temperature especially in the presence of catalysts. Piperidine (5 parts per hundred parts DGEBA) was added to d-DGEBA at room temperature and served as a catalyst. The material was cured at 160°C for 20 hours. Infrared measurements of intensity for the epoxide band at 915 cm^{-1} indicated that the cure was almost complete.

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

The most striking feature observed in the SANS results was the shift of the scattering peak position to lower q during cure. This implies that the average radius of gyration of the monomer molecules is increased by crosslinking. This result is rather surprising in light of our current understanding of rubber elasticity theory.

The other interesting feature was the sharpening of the scattering peak during crosslinking. The half widths of the peak changes from $0.36\ \text{Å}^{-1}$ to $0.25\ \text{Å}^{-1}$ when the sample cured. In addition, the ratios of the half-widths to the peak positions for the uncured and cured materials are 0.69 and 0.76, respectively. This sharpening of the scattering peak suggests that the crosslinking results in an enhanced correlation between neighboring, but not immediately connected, monomer units.

In summary, the crosslinking process in the thermoset system tested produced pronounced changes in the scattering behavior. These changes indicate 1) an increase in the radius of gyration of the monomer chains upon crosslinking, 2) an enhancement of the inter-monomer correlation. To further examine these questions, experiments are currently underway using a commercial resin, bisphenol A dicyanate, which is a good model system since it is a relatively pure material.

Infrared Measurements on Epoxy Networks Deformed in the Glassy State

Optimization of the mechanical performance of thermoset resins requires an understanding of deformation mechanisms at the microstructural level. However, the chain orientation behavior of networks deformed in the glassy state has received scant attention, and consequently little can be said regarding the molecular origin of mechanical properties in thermosets. As a means of addressing this problem, we have measured the microstructural orientation of a series of epoxy networks deformed in the glassy state using infrared dichroism.

The glassy networks of this study consisted of units of diglycidyl ether of bisphenol A (DGEBA) cured with four types of Jeffamines. Samples were subjected to compression between two surfaces, and the orientation of network segments at one of the surfaces was measured using attenuated total reflection-infrared spectroscopy (ATR). Dichroism was determined by obtaining polarized spectra both parallel and perpendicular to the direction of deformation.

Dichroic ratios were converted to second moment orientation functions, $P(\cos\theta)$, and were plotted according to the equation,

$$\ln\left[P(\cos\theta)/(\gamma^2 - 1/\gamma^2)\right] = \ln(1/5N_o) - k(\lambda - 1)$$

λ is the deformation ratio, N_o is the number of equivalent freely jointed links per active chain in the undeformed state and k is a material constant.

Plots of $\ln[P(\cos\theta)/(\lambda^2-1/\lambda^2)]$ versus $\lambda-1$ have been found to be linear for poly(methylmethacrylate) and polycarbonate in the glassy state. The same relationship holds true for deformed epoxy networks beyond the initial period of inhomogeneous deformation. Thus, the orientation behavior for these glassy networks coincides with the orientation behavior of linear polymeric glasses, and there is no direct perturbation on this mechanism arising from the presence of crosslinks. This strain behavior was interpreted according to a network unfolding scheme in which chain cohesion points gradually dissipate as the network unfolds with deformation.

Gel Spun Films and Fibers

Like polyethylene, poly(vinylalcohol) (PVA) is a flexible chain polymer capable of forming high strength/modulus fibers. PVA is a crystalline polymer for which the local conformation is not well understood. One expects that intra- and inter-chain hydrogen bonding play an important role in local chain organization. On deformation, hydrogen bonds may work as crosslinking points or entanglements. Since PVA is a polymer widely used in industry; e.g., fibers, staples, asbestos alternatives, sheet, high oxygen barrier film and so on, it is worthwhile to explore chain asymmetry of deformed PVA fibers and/or films.

Small Angle Neutron Scattering Studies on Chain Asymmetry of Coextruded PVA Film

This work examines the radii of gyration of solid state co-extruded PVA film cast from aqueous solution. Small angle neutron scattering measurements were made in directions both parallel and perpendicular to the direction of extrusion. The films were coextruded with a polyoxymethylene billet at 165-170°C using a crosshead speed of 1 mm/s.

The SANS results can be summarized as follows: the statistical segment length for PVA is found to be 5.76 Å. Chain asymmetry of solid-state coextruded PVA was examined by both a small-angle neutron scattering and birefringence measurements. It was found that the PVA chains were affinely deformed for extension up to a draw ratio of about 5. Birefringence measurements also show the affine nature of the deformation of PVA chains at the molecular level.

Physical Gels of Aqueous PVA Solutions - A Small Angle Neutron Scattering Study

High strength/modulus fibers of PVA are manufactured via a gel spinning process. The gelation process is produced by changing the temperature and involves physical rather than chemical changes. The work here is aimed at characterizing the molecular origin of the physical gelation process, and hence shedding light on the fundamentals of the formation of high performance fibers.

SANS data were collected on PVA gels as they were heated through their sol-gel transition temperature. The PVA solutions were tested using concentrations throughout the range near ϕ^*, the threshold concentration at which the polymer chains start to overlap. Mass fractal dimension and correlation length were extracted from the SANS data. Very little change in these two quantities were observed during the transition for solutions with concentrations greater than ϕ^*. In addition, the scattering intensity at $q > 1/R_g$ (R_g is the radius of gyration) also remained unchanged. These results suggests that the formation of the physical gel in PVA aqueous solution is a weak clustering process. The term weak is used here to mean that gelation does not introduce any significant disturbance to the polymer segment distribution in solutions. Such a disturbance is implied in other models like the fringed micelle model.

For the solution at concentration equal to ϕ^*, a maximum was observed in both the correlation length and the zero angle scattering intensity as the solution passed through the transition temperature. The origin of this maximum is interpreted successfully in terms of a two-phase weak clustering model.

Characterization Methods for Thick Section Composites

The growing interest in the private sector and other government agencies in structural designs that utilize polymer matrix composites in thicknesses from 10 cm to 30 cm or more requires the development of methods that can characterize the material in the interior of such a composite without destroying it. Starting from basic physical and chemical principles, and not allowing cost or engineering difficulties to eliminate possibilities, 20 different methods were identified and assessed. These methods included penetrating radiation, sonic waves, embedded sensors, and electrical measurements.

The composite features of highest interest include the mechanical properties (i.e. the elastic behavior of both the composite and the matrix), the absorption of water or other fluids, factors such as fiber volume fraction, matrix density, and voids, and residual stress fields. Those methods that have a high potential for yielding information on these features were identified.

PERFORMANCE

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The main thrust of the research effort on performance during the past year was damage tolerance. The work falls into four areas: resin toughness, characterization of interlaminar fracture behavior, analysis of delamination growth under compressive loading, and a small program on data base considerations. The research covers the complete range from the basic material properties to failure in simple structures such as delaminated plates.

Resin Toughness

The research on toughness focuses on two topics. First, the micromechanics of fracture in toughened resins were investigated by monitoring the growth of the crack-tip deformation zone in monolithic samples which are loaded to failure. Second, the effects of physical aging on fracture behavior were studied.

Toughening of Thermoset Composite Resins

Previous work at NIST has shown the importance of the deformation zone at the crack tip in determining both the fracture energy of a resin and the interlaminar fracture energy of its composite. The growth of this zone has been monitored in selected situations, and the results were used to explain effects such as the dependence of adhesive bond fracture energy on bond thickness when toughened adhesives were used. Although the number of tests was limited, the data suggested that the details of the failure process were quite complex, with different zone growth patterns obtained for different geometries and slow (or subcritical) crack growth proceeding the onset of rapid crack growth. To understand the failure behavior of toughened systems, failure events need to be studied in more detail.

To address this challenge, a comprehensive program has been developed to monitor the zone growth characteristics in a series of resins with a wide range of fracture energies. Simple compact tension specimens were made and loaded to failure at a constant crosshead speed. A stereo microscope with an attached video camera was used to record the development of the crack-tip deformation zone and the amount of subcritical crack growth. Load and displacement were recorded, and a stopwatch feature on the video system was used to assure synchronization of events.

Preliminary data suggest a number of interesting results. First, there was usually no clear onset point for crack growth, but rather a gradual acceleration. Consequently, it is difficult to establish a failure criteria based on the onset of crack growth. Second, there is a close association between the first observation of crack growth and the first obvious nonlinearity in the load displacement curve. Third, with the toughest materials tested, there is no unstable crack growth but only steady growth at a relatively constant velocity. In these tests, the size of the deformation zone ahead of the crack tip is relatively constant while the crack propagated. A more detailed analysis of the data is now underway and is expected to reveal a great deal about the failure of toughened thermoset resins.

Physical Aging and Fracture Toughness of Epoxy Network Glasses

As a part of a continuing program to investigate the effects of physical aging on the mechanical response of polymeric glasses, a series of experiments were performed to measure the fracture toughness of the glass as a function of the time after a quench from above the glass transition temperature, T_g, to various temperatures below T_g. The effects of three parameters were examined. First, the test temperature relative to the conventionally measured glass transition temperature was varied. Second the effects of aging time at each test temperature on the fracture toughness were studied. Third, the crosslink density of the glass was altered in order to study the effects of this parameter on the fracture toughness.

Preliminary results have shown that at more than approximately 30°C below the T_g of the system, the fracture toughness changes very little with aging over the range of aging times studied (>1000 h). On the other hand near the T_g, a factor of two decrease in the toughness of the glasses after aging was found. This explains, at least partially, the apparent disparity in results from various literature studies, i.e. some find that aging affects the fracture toughness and others report that it does not.

In future work, the yield strength of the epoxy networks will be characterized as a function of these same parameters. In this way, the influence of the yielding behavior of the networks on fracture toughness can be studied simultaneously with the effects of aging on the yield behavior.

Interlaminar Fracture Energy

Interlaminar fracture is a critical part of research on damage tolerance. During the past year, two topics were examined. First, experiments were conducted to help establish test methods to characterize interlaminar fracture behavior. Second, these methods were used to determine the interlaminar fracture toughness of laminated composites under mode II and mode III loadings. Emphasis was placed on providing a meaningful interpretation for such effects as nonlinearity of the load-displacement curve and fiber bridging, as well as on the determination of the mechanisms for energy dissipation at the crack tip.

Test Method Development

The development of test methods to determine the interlaminar fracture of composites is of continuing interest because of the importance of this property in applications. As part of the effort in this area by ASTM and VAMAS (Versailles Project on Advanced Materials and Standards) working groups on composites, tests were carried out to evaluate the influence of the method used to start the crack. Both mode I and mode II loadings were considered. A series of composite samples were prepared containing inserts of 0.5 mil, 1 mil, and 2 mil thickness, some sprayed with a release agent prior to insertion in the laminate to minimize adhesion. In addition, for some samples the crack was advanced a short distance beyond the insert before testing as a way to simulate a natural delamination. A number of methods for this crack extension were examined.

The tests were performed using a common epoxy based system and a thermoplastic material. The results show that the "initiation" and "resistance" fracture energies greatly depends on the insert used and the precracking method. As might be expected, the best (i.e. lowest) results were obtained with the thinnest (0.5 mils) sprayed with release agent.

Interlaminar Shear Fracture of Laminated Composites

Most research to date on interlaminar fracture has focussed on mode I, which proved to be the critical failure mode in the first-generation, brittle-matrix composites. The use of tough matrix systems, however, has greatly improve the damage tolerance of composites. The accompanying reduction in ratio of mode II to mode I fracture toughness, G_{IIC}/G_{IC}, for such materials necessitates the consideration of the shearing modes in any fracture analysis. Although research on mode II interlaminar fracture has grown considerably over the last few years, a few issues require attention. These include the need for a meaningful interpretation of the observed nonlinearity in the load-deflection curve and fiber bridging at the crack tip.

The mode II and mode III interlaminar fracture energies of a number of advanced composites were studied using beam type test specimens and scanning electron microscopy to examine the fracture surfaces. The fracture energies in mode II were independent of crack extension while those for mode III exhibited a "resistance" behavior (increase with crack extension) that was attributed to fiber bridging. The initiation fracture energy, considered here as the true measure of G_{IIIC}, coincided with G_{IIC}. For either fracture mode, the interlaminar region ahead of the crack tip exhibited considerable plastic deformation, and this is believed to control the laminate toughness. The interlaminar fracture energy in shear was found to be accurately predicted from a straightforward adhesive joint test provided the adhesive thickness coincided with the thickness of the interlaminar resin layer. This is identical to the previous result for mode I loading where the adhesive test was shown to be a valuable substitute for tests on the composite. The adhesive test has the advantage that fiber bridging is not a problem, and the test can be performed with very small amounts of resin.

Analysis of Laminate Compression Failure

Debonding of a thin surface layer ("film") from the main loading-bearing body is a failure mode that is of interest in a variety of technological applications, including delamination of composite materials and decohesion of adhesively-bonded coating layers. The model previously developed has been extended to give a simplified mixed-mode fracture analysis combining nonlinear thin-plate stress solutions with crack tip elasticity results. This analysis can account for local variations of G_I, G_{II} and G_{III} in thin-film debond problems associated with large deformations. Of particular interest in this study was the modelling of compression failure in laminated composites following impact by foreign objects.

A one-dimensional and an elliptical plane-form crack were considered. The analysis assumes that the film thickness is very small compared to the in-plane dimensions of the crack, and that the dimensions of the delaminating area are small compared to the dimensions of the substrate. Deformations were induced either by a transverse pressure or a biaxial-compression or tension stress field. The film was treated as a thin plate with clamp type boundary support. The deformation and stress behavior of the plate was determined from a Rayleigh-Ritz type energy approach, with the strain-displacement relationship being in accordance with von Karman's thin plate theory. Convergence of the plate solution was assessed by increasing the number of terms in the assumed polynomial series for displacement. As many as 77 displacement terms were used to insure that the bending and membrane stresses were accurate to within ±1 percent. Comparison with more rigorous analyses indicates that the present model is quite effective if the film thickness is at least an order of magnitude smaller than the in-plane dimensions of the debond.

The results identified explicitly the material and geometric parameters controlling crack propagation or arrest in both uniaxial and biaxial compression. The analysis can therefore serve as a basis for designing composites and adhesively-bonded parts that resist delamination failure. Because there is a wide range of mode interaction, and the load application is relatively easy; the debond configurations analyzed may also serve as a means for evaluating mixed-mode fracture toughness of composites or adhesive bonds.

Composites Databases for the 1990's

A database draft standard for the identification of polymer matrix composite materials and for reporting test results was prepared. The draft standard is based on a comprehensive description of the flow of data through the polymer matrix composites community.

Two essentially different kinds of databases are required, one oriented toward a particular group of data users, and one designed to make the collection of all kinds of relevant data straightforward. An interactive dictionary to serve as a tool in the development of the best names is described. Relationships between the draft standard and various groups concerned with composites are noted.

This work was supported by the Strategic Defense Initiative Organization, and performed in cooperation with the ASTM Committee E49, the Military Handbook 17 project, and DOD contractors concerned with data on advanced composite materials. The draft standard and supporting information are described in a report "Composites Databases for the 1990's", (NISTR# 88-4016) authored by Darrell H. Reneker, John M. Crissman, and Donald L. Hunston. Over 350 copies of this report have been distributed.

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 solution properties. Polymer molecular weight SRM's are 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, furniture, packaging materials, housewares, toys and clothing materials. Materials are also produced from polymer/solvent systems with solvent removed during or after processing. Examples of such systems include wet spun fibers and non-woven fabric.

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 a 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 retardant, processibility, and barrier properties can be improved through blending. High cost engineering plastics with special properties can often be obtained by the blending of 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. Major factors which are important to the understanding of the production of desirable heterogeneous blends are: (1) a better knowledge of the fundamental factors that control blend morphology, interfacial adhesion and the relationship between the phase demixing kinetics and the equilibrium thermodynamics of polymer blends; (2) a better understanding of the influence of the flow field on the mixing and demixing processes; (3) the solution properties of polymers. In the context of the objectives of the Group, solution properties are important not only for processing technology development, but also for Standard Reference Materials production.

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 effect 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. 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 allows an extension of the study to structures of larger size is currently under construction.

FY 89 Significant Accomplishments

- Phase diagrams of polymer solutions and melts under shear were measured using a specially constructed couette geometry shear cell. For a polystyrene and polybutadiene blend dissolved in dioctyl phthalate, a depression of the spinodal temperature was observed for all shear rates examined. The results indicate shear induced mixing and are in qualitative agreement with results obtained by other methods.

- The 10-meter SAXS Facility had active outside users which includes 4 industrial laboratories, 3 academic institutions, and 3 activities involving other federal laboratories. Activities of users include: studies on the effect of processing conditions on the final state of polyethylene films, studies of the relationship between the amorphous and crystalline phases in semicrystalline polymers, and studies of the effects of compression deformation on the fibers in a composite.

- Blends of linear protonated polystyrene and crosslinked deuterated polystyrene has been studied by small angle neutron scattering. It was found that linear chains can be incorporated into networks formed by sequential polymerization of the network surrounding the linear component (i.e. single phase blend of linear and crosslinked polymers) if the network density is kept low. This result helps to explain why similar systems studied in the past at higher crosslink densities have almost always phase separated at some point during the synthesis.

- A simple model was developed which qualitatively describes the effect of surface roughness, which can often be quantified through measurement of the fractal dimension of the surface, on the properties of surface interacting polymers. The model has application also to natural occurring surfaces (cell membranes and organelles, soils and rocks, etc.) which are highly irregular, appearing on average "similar" in roughness over a large range of observational scales.

- A standard reference material for melt flow rate was certified. The polyethylene, SRM-1474, material with a melt flow rate of 5.03 g/10 min will be used to check equipment stipulated by the ASTM D-1238 voluntary standard.

- The tracer diffusion coefficient of anthracenophane has been measured in various polymer matrices (polystyrene 422K, 2.8K, poly(vinylacetate), poly(vinylmethylether), polystyrene 422K with trace solvent) over a wide temperature range. The temperature dependence of the dye diffusion coefficient is found to be universal once the diffusion coefficient in each polymer matrix is scaled to the diffusion coefficient at the reference state of the glass transition temperature of the polymer matrix. A significant annealing effect on dye diffusion has been observed near glass transition temperature, which is attributed to slow rearrangement of polymer matrix.

EXPERIMENTAL

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Microstructure and Isotopic Labeling Effects on the Miscibility of Polybutadiene Blends Studied by the SANS Technique

Deuterated polybutadiene and protonated polybutadiene (PBD/PBH) blends with various microstructures have been studied by the small-angle neutron scattering experiments. Correlation length, ξ, zero-wavenumber structure factor, S(q=o), and interaction parameter, χ_{blend}, has been successfully separated into χ_1 (interaction parameters between the same isotope labeled 1,2-unit and 1,4-unit) χ_2 (opposite isotope labeled 1,2-unit and 1,4-unit), and χ_3 (opposite isotope labeled 1,2-unit with 1,2-unit or 1,4-unit with 1,4-unit). More experiments are being conducted to remove the assumptions used in this study. Also studies on polybutadiene/polyisoprene blends of various microstructures are in progress.

Chain Conformation of a Block Polymer and a Part of a Block Polymer in a Microphase-Separated Structure

The radii of gyration of a polystyrene block along the directions parallel and perpendicular to the lamellae within the lamellar structure of poly(styrene-b-2-vinylpyridine) were measured by using small angle neutron scattering. It was found that the block polymer extends along the perpendicular direction, while it shrinks along the parallel direction. The extension is in accord with theories of microphase-separated structure, but no theory can predict the shrinkage. From the molecular weight dependencies of radii of gyration along the parallel and perpendicular directions it is concluded that the block polymer shrinks along the parallel direction to preserve the same intermolecular interactions in lamellar structures as in disorder states. Also SANS has been used to measure the chain conformation of parts of the polystyrene/poly (2-vinyl pyridiene) diblock copolymer. It was found that the part of the chain at the free end of block polymer is unperturbed and located in the middle of domain, while the part of the chain adjacent to junction point between the two blocks is located near the domain boundary and shrunken relative to the unperturbed dimension, along the direction parallel to the lamellae.

The Effect of Radiation Crosslinking on the Scattering Function in Weakly Interacting Miscible Polymer Blends

Using small angle neutron scattering (SANS) the scattering function in the single phase region of the phase diagram was measured for the weakly interacting polymer blend system of protonated polystyrene (PSH) and deuterated polystyrene (PSD) which had been crosslinked by gamma rays from a cobalt 60 source. A theory presented by de Gennes for the critical scattering from crosslinked blends and the effect of crosslinking on the phase diagram had been tested previously using SANS with the strongly interacting blend system poly(vinyl methyl ether)/PSD. In the crosslinked PSH/PSD system the measured scattering function was found to be essentially unchanged from the scattering function measured for the uncrosslinked system. There is no peak present as predicted by the theory, although there is a small decrease in S(0) (the extrapolated zero angle scattering) after crosslinking. The same results were observed initially with the PVME/PSD system though a peak did subsequently appear upon changing the temperature (changing χ). In the PSD/PSH system there is no temperature dependence of χ. Combining these observations with the results from the PVME/PSD system the conclusion can be drawn that the theory does not predict the scattering observed after crosslinking if χ remains roughly constant but does predict the observed behavior qualitatively when χ is subsequently changed, as for example by changing the temperature.

SANS Studies of Blends of Crosslinked PSD with Linear PSH

Small angle neutron scattering (SANS) has been used to study the scattering function and thermodynamics of blends of linear protonated polystyrene (PSH) and crosslinked deuterated polystyrene (PSD). Two series of samples were synthesized. Series 1 was a set of samples with the same network (N_c=387, where N_c is the average number of monomer units between crosslinks) but varying the length of the linear chain (N_b=91, 308, 422, 981, 1711 and 3413, where N_b is the number of monomer units in the linear chain). Series 2 was a set of samples containing the same length linear chain (N_b=422) but varying the network density systematically (N_c= ∞, 960, 475, 345, 260, 158). In the series 1 samples, as the length of the linear chain is increased the SANS scattering increases as the sample approaches phase separation. This is because as the length of the linear chain increases the entropy of mixing decreases until it can no longer balance the unfavorable elastic contribution from the network and phase separation occurs. In the series 2 samples, the scattering increases as the network density increases (N_c decreases) because the elastic contribution to the free energy is getting larger until it overwhelms the mixing portion of the free energy and phase separation occurs.

In conclusion it has been found that linear chains can be incorporated into networks formed by sequential polymerization of the network around the linear component (i.e. single phase blend of linear and crosslinked polymers) if the network density is kept low (N_c>150). This result helps to explain why similar systems studied in the past at higher crosslink densities have almost always phase separated at some point during the synthesis. SANS can be used as a tool to study the thermodynamics of these systems and values for the elastic contribution to the free energy can be calculated from the extrapolated zero angle scattering.

Small Angle X-ray Scattering of MDI/BDO Based Polyurethanes

Small angle x-ray scattering (SAXS) is used to study the deformation behavior of polyurethanes. Upon deformation the hard segment domains are observed to orient first with their long axis perpendicular to the draw direction. At larger deformations (>200%) the hard segment domains begin to break down which increases the phase mixing between the hard and soft segments and results in a decrease in the scattered intensity. Currently, a deformation stage for in situ experiments in the Polymers Division's 10m SAXS camera is under construction which should allow both deformation and relaxation experiments on the same sample. This information is needed to understand both the phase mixing and demixing processes that occur with the application and release of strain in these polyurethanes.

Universal Temperature Dependence of Dye Diffusion in Polymer Matrix Near and Above Glass Transition by Forced Rayleigh Scattering

Utilizing the wide dynamic range of forced Rayleigh scattering technique, the tracer diffusion coefficient of anthracenophane has been measured in various polymer matrices (polystyrene 422K, 2.8K, poly(vinyl acetate), poly(vinyl methyl ether), polystyrene 422K with trace solvent) over a wide temperature range. The temperature dependence of the dye diffusion coefficients in all the polymer matrices can be well represented by the WLF equation. It was found that the temperature dependence of the dye diffusion coefficient is universal after the temperature is scaled to the reference state of the glass transition temperature of the polymer matrix. A significant annealing effect on dye diffusion has been observed near glass transition temperature, which can be attributed to slow rearrangement or packing of polymer matrix itself. This work has currently been extended to the measurement of the tracer diffusion of dye below the glass transition temperature of the matrix.

Shear Effects on the Phase Separation Behavior of Polymer Blends in Solution and in Bulk by SANS

Measurements were conducted using a specially constructed couette geometry shear cell which permits in situ studies of sheared polymer solutions and melts. Two different systems were examined: 1) polystyrene and polybutadiene dissolved in dioctyl phthalate and 2) polystyrene and poly(vinyl methyl ether). For the blend dissolved in solvent, a depression of the spinodal temperature (T_{sp}) was observed for all shear rates examined. At a maximum shear rate of 2000 s^{-1}, the shift in the T_{sp} was approximately 25° parallel to the flow direction. Perpendicular to flow, a shift in T_{sp} of approximately 10° was observed. The results indicate shear induced mixing and are in qualitative agreement with results obtained by other methods. For the polymer blend without solvent, shifts in T_{sp} were also observed. At a maximum shear rate of 1 s^{-1}, a shift in the spinodal of 10°C was observed parallel to flow. No effect was observed perpendicular to flow. These results indicate shear induced mixing as well as a decoupling of shear effects in different directions relative to the flow field. Work is in progress to relate the effects of shear to the steady shear viscosity behavior of the blends.

Self-Calibrating Gel Permeation Chromatography

Gel permeation chromatography (GPC) is a widely used technique for estimating the molecular weight distribution (MWD) of high polymers. However, the usefulness of the conventional GPC apparatus is limited by the need to provide, for each polymer to be measured, calibrants of known molecular weight over the entire molecular weight range in which the MWD is significantly different from zero. The calibration depends, among other things, upon the chemical nature, degree of branching, etc., of the polymeric material, so that each new material requires a fresh calibration. The frequently-used "universal calibration" hypothesis is limited to comparisons of polymers of similar shape, and is not suitable for quantitative determinations. Some instruments circumvent the need for calibrants by adding a single-angle light scattering detector to the usual concentration-sensitive detector. However, this does not allow the extrapolation to zero scattering angle which is required, in principle, to relate scattering intensity to molecular weight. In addition, qualitative information about the variation of scattering with angle, normally needed for assurance that the results obtained are meaningful, cannot be obtained from single-angle measurements.

A light-scattering detector for the GPC has been designed and constructed which measures, in real time, scattered intensity over a range of scattering angles. The apparatus is computer-controlled in a way that allows scattered intensity to be measured as a function of both scattering angle and concentration. Continuous monitoring of the variation of scattered intensity with angle while the chromatogram is being obtained allows immediate identification of problems such as association, microgel formation, etc. which would affect the validity of the molecular weights obtained, an important consideration for work on new and unstudied materials. Use of this detector makes the GPC "self-calibrating" in effect, by using the unknown samples to determine the calibration parameters of the GPC columns. The new detector has been tested by measuring a series of linear and branched polystyrenes. The results confirm its ability to "self-calibrate" the chromatograph for linear materials. They also demonstrate its ability to detect crosslinking in non-linear materials, and to establish calibration curves for star-branched samples, which suggests that this instrument will be useful for studies of branched systems.

Failure of Latex Barrier Films

The failure of latex barrier films is of commercial and medical interest. Regions with low local crosslink density may be expected to fail before the rest of the film fails under certain loading conditions. The change in the crosslink density across the film was determined by measuring the change in local swelling using a fluorescence microscope and a FTIR microscope.

The stress to failure of rubber is known to decrease dramatically as a result of the addition of a small amount of swelling agent. The swelling behavior and stress to failure of these barrier films after immersion in body fluid simulants has been studied. The work on latex barrier films is supported by FDA.

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. The Polymers Division and NARA have developed a research program to study the protection mechanism provided by containers commonly used in protecting archival materials from atmospheric pollutants. Also, the degradation mechanism of paper by these pollutants and the relation of the degradation mechanism to various possible storage modes are under study.

THEORY

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

Effect of Surface Roughness on Polymer-Surface Interactions

Many naturally occurring surfaces (cell membranes and organelles, soils and rocks, etc.) are highly irregular, appearing on average "similar" in roughness over a large range of observational scales. The irregularity of such surfaces can often be quantified through the measurement of the fractal dimension d_{fs} of the surface. In three dimensions, values of d_{fs} near 2 correspond to relatively "smooth" surfaces while surfaces having values $d_{fs} \approx 3$ are relatively "rough" and space filling. A simple model is introduced to qualitatively describe the effect of this kind of surface roughness on the properties of surface interacting polymers and comparison is made with recent Monte Carlo data and renormalization group calculations. The model indicates that increasing the surface irregularity (i.e., the fractal dimension d_{fs}) has the effect of enhancing polymer-surface interactions relative to an idealized planar interface of infinite extent. This is a consequence of a greater probability of polymer-surface intersection with increasing roughness. It is also argued that adsorption occurs more readily on fractal surfaces since adsorption on rough surfaces requires the loss of fewer degrees of freedom than for a smooth surface. A rough surface may adsorb a polymer when a corresponding smooth surface of the same material will not adsorb. Roughness can thus alter the effective polymer-surface interaction in a fundamental way.

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 interactions complicate the interpretation of these dimensionless ratios in practice and conditions and properties which minimize these complications are identified.

Relaxation in Disordered Materials with Application to Polymer Melt Dynamics

Classical models of viscoelastic materials neglect memory effects which can have a significant effect on relaxation in disordered condensed materials. 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.

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.

Glass Transition as a Function of Molecular Architecture

The molecular architecture of polymers can be changed by forming stars, rings, branching, crosslinking and the various kinds of copolymers (block, random, condensation) either singularly or in combination. The Gibbs-Di Marzio entropy theory of glasses is being used to predict the variation of glass temperature for these systems. The general rule has been discovered that any change of molecular architecture that lowers the configurational entropy raises the glass temperature and conversely. This rule is useful for qualitative understanding of glass formation. Quantitative comparisons with experiment are being attempted.

The Time and Temperature Dependence of Viscosity in Polymer Liquids

It is observed that the diffusion coefficient of small tagged molecules in bulk polymer and the inverse viscosity of the polymer have the same temperature behavior. This suggests that there is a fundamental process underlying both phenomena. The velocity autocorrelation function of a bead immersed in polymer is of primary importance since it is known to be proportional to the diffusion coefficient. An attempt is made to calculate it by examining the diffusion of a phase point over the potential energy surface in configuration space. The stretched exponential time dependence of polymer relaxation is then determined by relating diffusion in real space to that in phase space (configuration space). The temperature dependence is determined by modifying an argument due to Adams and Gibbs.

Elasticity in Liquid Crystals and Membranes; Crystallization Kinetics

Commonly used expressions for the strain energy in bent membranes are inadequate because they leave out the compressive and extensive contributions to the strain energy. These are significant whenever the geodesic curvature is non-zero. The formalism for treating this problem is examined. Results are necessary to proceed with the development of crystallization kinetics. Under certain conditions twisted crystalline ribbons (like the stripes on a barber's pole) are possible structures. The finite width of the ribbons arises from strain buildup at the edges. The kinetics of growth of curved crystalline membranes is being developed in conjunction with Jerome Lando of Case Western Reserve.

STANDARD REFERENCE MATERIALS

C. H. 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, a program was initiated to produce polyurethane Standard Reference Materials (SRM's) and to develop improved methods for characterizing these and other block copolymer systems.

Two polyurethane SRM's are being produced with weight-average molecular weights determined by ultracentrifugation, and with limiting viscosity numbers determined under the conditions commonly used for the estimation of MWD by gel permeation chromatography. These SRM's are not the usual commercial polyurethanes, but rather are model compounds to which the usual techniques for determining molecular weights of homopolymers can be applied. Methods are being developed for estimating compositional variation in polyurethanes, both for checking our own SRM's and for investigating the range of variation in commercial polyurethanes. During FY 89 measurements leading to the certification of the low molecular weight material were initiated.

Poly(methyl methacrylate) Standard Reference Materials

Measurements of the weight average molecular weight of SRM 1487, a low molecular weight poly(methyl methacrylate), (PMMA) by ultracentrifugation were finished this year. A certificate for the material has been issued. This completes the certification of the three PMMA standard reference materials. This work was supported by the Navy and OSRM.

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. Previously NIST polymer SRM's all had melt flow rates of less than 2 g/10 min. Additional polyolefin standards were needed for melt flow rates higher than 2 g/10 min.

A polyethylene, SRM-1474, with a melt flow rate of 5.04 g/10 min was certified this year. This work is supported by OSRM.

A polypropylene with a melt flow rate of about 12 g/10 min is being considered for certification 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 is currently being negotiated with 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 applications such as adhesives, coatings, paints, lubricants, oil resistant plastics, etc. The need for such standards for these materials has been noted by Visiting

Committees, during staff visits to industrial characterization laboratories, and in the responses to market surveys.

By far the most pressing need for water-soluble molecular-weight polymer SRM's is for calibration standards for aqueous size exclusion chromatography (SEC). For this purpose, samples of narrow molecular weight distribution are to be preferred.

Work has begun on the certification of two narrow molecular weight polyethylene oxides, one in the 30,000 to 60,000 molecular weight range and another in the 100,000 to 300,000 molecular weight range. The polyethylene oxide SRM 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 4 industrial laboratories and 3 academic institutions. There are also 3 activities involving other federal laboratories.

Activities by internal NIST Users have focussed on polyurethane materials, metal uptake in bacteria, graft copolymers, and matrix materials for composites.

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

a) Experiments to test the Vonk calculations for the three pinhole geometry are being conducted. Results to date indicate that the second and third pinholes must be somewhat smaller than predicted to allow for the irregular shape of the focal spot. The results do, however, indicate that increased intensity can be obtained if attention is paid to pinhole selection.

b) Cross-correlations of intensity data with neutron scattering results have been performed on a few secondary scattering standards. Data acquisition procedures now incorporate data acquisition on secondary standards as part of the normal chain of events, thus permitting later rescaling to absolute intensities.

c) Image processing software to eliminate image artifacts and to correct for electronic resolution is being developed. This will permit calculation of invariants, correlation functions, and orientation functions. Preliminary tests indicate that such processing may have to be carried out on the NIST supercomputer.

Additional software development work aimed at providing programs that users can employ on economical workstations at their home locations has been initiated. The principal barriers to such development arise from difficulties in programming for the WIMP (Window, Icon, Menu, Pointer) user interfaces found in modern desktop personal computers.

A collaborative effort with Dr. Edward S. Clark of the University of Tennessee pursues research into methods for measuring orientation distribution functions for materials exhibiting small-angle scattering. Although the pole-figure method is well established for wide-angle diffraction, the methods used there cannot be transferred directly to small-angle scattering because of the absence of crystalline order in the latter case.

X-Ray Pole Figure Facility

Recent effort on this facility has been directed toward making the data more quantitative. A study of absorption effects in polyethylene by Research Associates from Mobil Chemical Company revealed that these effects cannot be ignored. A literature survey revealed that existing software codes for dealing with this problem are not appropriate for the sample geometry that is most effective in the NIST facility.

Corrections for background and peak overlap are other issues that need attention. Energy-dispersive detection systems appear to offer promise for substantial improvements along these lines.

Software for calculating Orientation Distribution Functions has been obtained from Dr. John Kallend of the Illinois Institute of Technology. This approach to reducing the data appears to offer promise for improved calculations of properties and modelling of the orientation. Implementation of these procedures cannot be completed until the correction problems mentioned above have been solved.

DENTAL AND MEDICAL MATERIALS

The objective of the Group is to provide basic materials science, engineering, and test methods which may be used by sectors of the health-care industry 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, aimed at development of materials and techniques for promoting adhesion to tooth, dentin, enamel, bone, and soft tissues, are pursued for reducing marginal leakage of restorations. 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 cements 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 with finite element stress analysis for evaluation of the reliability of dental systems.

Techniques for characterizing the effects of compositions on the casting behavior of alloys are being published with a view toward improved alloys and processing methods.

A multidisciplinary effort on the use of microwave generated gas plasmas for sterilization of medical and dental instruments may result in improved health care delivery in the future.

FY 89 Significant Accomplishments

- A patent was applied for on the use of microwave generated gas plasmas for sterilization of dental and medical instruments in 30 seconds at temperatures near or below 60°C.

- Microcrystalline glass formulations with intrinsic tooth-like colors were fabricated for use as "megafillers" for dental composite restorations.

- An intraoral device was developed to protect patients from secondary radiation emanating from metallic restorations during radiation cancer therapy.

- Multifunctional oligomers which polymerized by cyclopolymerization yielded highly crosslinked polymers with high degrees of conversion. Favorable results were obtained when they were substituted for BIS-GMA in dental composite formulations.

- An algorithm was developed for predicting the service life of dental prostheses based on limited clinical failure data.

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

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In collaboration with the American Dental Association at NIST, pin and disc wear measurements were made on synthetic enamel (sintered polycrystalline hydroxyapatite used to simulate human enamel) against titanium, which has potential application as a posterior restorative. Of particular concern is the extent of wear on the enamel surfaces of teeth opposing those with the restorations. The in vitro wear results were compared with corresponding ones using common commercial dental alloys which bracket titanium with respect to hardness. The wear of the Synamel disc correlated with the alloy-pin hardnesses except for Type II Gold where two distinct wear modes were observed from two competing processes. The two wear rates bracketed those using all of the other alloys, which displayed only one mode. As observed by optical microscopy, the low-wear mode resulted from the Synamel surface being glazed near the onset of wear. The high-wear mode resulted from the transfer of gold to the disc for which the gold-gold adhesion apparently produced a higher coefficient of friction commensurate with a larger wear rate. More work is necessary to determine the relevance of these phenomena to corresponding in vivo wear.

The development and construction of the second version of an automated, pin and disc (3-station) dental-wear apparatus has been completed. The principal distinctions between the two versions are that the second employs stepping motors, which facilitate speed control and accurate positioning for wear track-depth measurements, and keeps the specimens submerged in arbitrarily selected liquids during wear for relevant environmental studies. The apparatus is controlled by a microprocessor and requires no attention during wear and measurements at arbitrarily selected intervals. The wear measurements are accomplished by using linear variable differential transformers which make depth measurements at ten equidistant positions around the circumference of the wear track.

Clinical applications of dentin-enamel adhesive systems have continued. Application of a simplified two-step material has been included in the original trial and application to ceramic restorations as well as selected metallic restorations has been explored. Recall examinations of the original ferric oxalate based adhesive system have indicated a staining potential at the adhesive interface and these restorations are being replaced with the non-oxalate simplified system as stains appear. There are currently more than 300 restorations included in this trial.

The characterization of radiation scatter from dental amalgam, gold and NiCr casting alloy, and natural tooth structure when exposed to therapeutic ^{60}Co and 10 MeV photon sources has been completed. The dose-depth relationships at the tissue-metal interfaces have been completed on both the forward scatter and back scatter sides of these materials.

Clinical observations of precision-cast titanium crowns are now in their 46th month, and although minimal wear is apparent on occlusal surfaces of opposing teeth, general compatibility with oral tissues continues to appear excellent.

Microcrystalline glass formulation based on metastable beta quartz have been fabricated for evaluation as glass inserts in "megafilled" composite restorations. Tooth-like colors have been intrinsically developed in these glasses through the addition of metal oxides and various heat treatment regimens. These formulations, based on beta-quartz, have the possibility of exhibiting very low thermal expansion coefficients. Work is presently underway to determine the thermal properties of these glasses.

Modifications on a polymerization shrinkage dilatometer were completed for improved measuring precision, temperature stability, and ease of sample handling. A study using BIS-GMA based resin with varying filler content was conducted to assess the accuracy and reproducibility of the polymerization shrinkage results. Results indicated that the percentage of shrinkage is directly related to the percentage by volume of the resin content. Further analysis of the data may be useful in determining the effective filler density and extent of air entrapment with different filler sizes and compositions. The modified dilatometer will allow further studies using very low shrinkage or even expanding polymer composites.

MEDICAL MATERIALS, INSTRUMENTS AND DEVICES

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Patents relevant to a self-setting calcium phosphate cement, previously developed by ADAHF research associates in the DMMG, have been licensed to Osteogenics, Inc., which is developing the material for repairing bone lost in cranial surgery.

A patent has been applied for on the use of microwave generated gas plasmas for sterilization of medical and dental instruments. It was found that sterilization can be achieved with 30 second exposures on instruments such as dental burrs with only a 40°C temperature rise. The existing system has been upgraded with a new microwave oven and as improved, cleaner vacuum system to reduce outgassing impurities. Work has begun on the testing of the effects of the plasma on the material properties of dental instruments.

DENTAL POLYMER, COMPOSITE, CEMENT SEALANT, AND ADHESION CHEMISTRY

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Further research into resin- and/or polymer modified glass-ionomer cements has shown that some of the aqueous polymer solutions (e.g. polyethylene oxide) have surfactant properties which permit the formulation of cements with higher than usual powder/liquid ratios. Also, ionic monomers (e.g. calcium methacrylate) were shown to be effective modifiers of glass ionomer cements.

Previous research with dimer and trimer acids showed that they formed halatopolymeric cements when mixed with basic powders (e.g. $Ca(OH)_2$, ZnO, etc.). Hybrid dimer acid cement-composites also can be formulated with compatible monomers and/or polymers using techniques similar to those described for the hybrid cement-composites based on glass ionomer cements.

The synthesis of multivalent metal dicarboxylates based on PMDM (the diadduct of pyromellitic anhydride and 2-hydroxyethyl methacrylate) was shown to be feasible by several routes. The calcium and magnesium salts of PMDM were partially soluble in water whereas many others (e.g. Ca, Al, Zr) were insoluble. Salts containing redox metals (Ca, Fe, Ti had catalytic properties while those that were water soluble can be used in resin modified glass ionomer cements.

Adhesion testing on dentin-enamel adhesive materials continues with improvements in the formulations and packaging of commercial materials. Patent licensing of the simplified adhesive to Myron International, Inc. of Kansas City, Kansas, has resulted in the introduction of a market product based on the simplified two-step adhesive material. Methods of packaging and dispensing the treatment solutions were developed in conjunction with the transfer of this technology.

Testing of dentin bonding molecules has proceeded to reveal some fundamental aspects of the mechanism for dentin bonding. Under former conditions of bonding, the determination of which molecule was significantly better could not be made. A systematic variation of the concentration of one component from 10^{-7} Moles/Liter of acetone through 0.5 Moles/Liter has provided a quantitative evaluation of how much better some compounds can promote bonding to dentin. A further benefit of this protocol is that structural variations among molecules assayed in this scheme provides a description of the importance of certain functional groups to the bonding mechanism.

New, more reactive free radical ring-opening spiro orthocarbonate monomers were formulated into dental composite resins. The mechanical strengths of the photocured composites were equal to that of the BIS-GMA/TEGDMA control (rather than the 10-20% decrease in strength that was characteristic of formulations incorporating the less reactive spiro monomers).

The synthesis of a symmetrically substituted spiro orthocarbonate by a one-step procedure resulted in a liquid monomer suitable for cationic ring-opening polymerization with an expansion in volume.

The ring-closing cyclopolymerization of oxy-bis-methacrylate monomers was found to give polymers with higher degrees of conversion and significantly less polymerization shrinkage than conventional dimethacrylates. The synthetic procedure was dramatically improved over that initially used to prepare these unique monomers. Multifunctional oligomers capable of this same cyclopolymerization process were synthesized and polymerized to highly crosslinked polymers with high degrees of conversion. The substitution of these reactive oligomers for the BIS-GMA base monomer component of dental composite resins was evaluated with favorable results.

Elastomeric metal-polymer composites have been formulated from microspherical silver-copper alloy and polysiloxane polymer. At filler levels of 90% metal by weight, this material has demonstrated ability to block ^{60}Co radiation at reasonable thicknesses. This material can be readily formed or molded and has applications in the fabrication of shielding devices used during radiation therapy.

A near infrared (NIR) method has been developed to study the absorption of water by dental resins and composites. The extinction coefficient of water depends inversely on the extent to which the water is hydrogen bonded, which in turn depends on whether the resin itself can donate hydrogen bonds and whether the water in a particular polymer can form clusters so it can hydrogen bond to itself. The technique is sensitive enough for water sorption to be determined on thin films which equilibrate rapidly. Also, thin films can be stacked between calcium fluoride windows to make a thick sandwich using paraffin oil as spacer. The hydrophilicity of the resin can be estimated from the position of the NIR water absorption maximum. If the water content is also determined gravimetrically, the water content at which the water begins to segregate into clusters can be estimated from the change in the water extinction coefficient with water concentration.

CALCIUM PHOSPHATE CHEMISTRY, BIOCHEMISTRY, STRUCTURE AND CLINICAL IMPLICATIONS

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Based on previous data, it was hypothesized that the structure of stoichiometric hydroxyapatite containing about one water molecule per unit cell may be distorted from hexagonal to provide an additional lattice site to spatially fit this water. Experiments are in progress to test this hypothesis but are incomplete at present.

Chemical spectroscopic, and crystallographic investigations of octacalcium phosphate-polycarboxylate double salts were extended to include 17 carboxylates. Nine of these 17 carboxylates formed double salts. Included in these 9 are 3 carboxylates (succinate, fumarate, and citrate) that are also found in the Krebs cycle, the final metabolic step in the utilization of glucose as a energy source in the body. Whether any of these double salts have biological functions remains to be determined.

A patent application was filed, J. M. Antonucci, B. O. Fowler, and S. Venz, on 2/27/89 on the preparation and use of calcium metaphosphate as fillers for, dental, medical, and other composites. Beta calcium metaphosphate fillers with controlled surface porosities also can be prepared for improved interfacial bonding in composites.

Matrix vesicles are the sites of initial mineralization in many skeletal tissues, including dentin. Results from model liposome studies suggest that extracellular macromolecules such as proteoglycans may be contributing factors in the control of the subsequent spread of the first mineral clusters into the surrounding tissue matrix. Vesicle-like structures also appear to play a role in pathocalcifications such as occur in atherosclerotic plaques. Liposome studies revealed that cholesterol, an essential component of vesicle membranes and a major plaque component, may influence mineral formation in these pathological deposits by affecting transmembrane calcium movements.

A novel fluoride rinse system consisting of two solutions has been developed. Solution A contains a soluble calcium salt and a pH buffer; solution B contains a complex fluoride compound (sodium fluorosilicate) and a soluble phosphate slat. The fluoride uptake from this rinse was over 15 times greater than that from a conventional rinse having the same fluoride concentration.

Studies of the dissolution rates of calcium fluoride deposited on tooth surfaces by an acidulated phosphate fluoride (APF) treatment were undertaken. The results suggest that in topical fluoride treatments it may be desirable to form relatively large calcium fluoride crystallites on tooth surfaces so that protective coatings may form on the calcium fluoride crystals to prolong the beneficial effects.

A treatment procedure incorporating an alkaline calcium solution and an acidic phosphate solution was used to remineralize root lesions in vitro using thin human root sections containing artificially formed caries-like lesions. This treatment procedure and other experimental methods for rapid remineralization of teeth and desensitization of dentin are proving effective.

The extent of the reactions and compressive strengths of a previously developed self-setting calcium phosphate cement (CPC) were investigated as a function of time. The results showed that hydroxyapatite was the only reaction product and the reaction was nearly completed within four hours. The combination of self-setting and high biocompatibility makes CPC a highly interesting and useful material in a number of dental and medical applications.

Investigation of octacalcium phosphate (OCP) and its role in biomineralization was pursued. OCP-carboxylate systems were studied because of their formation of double salts. In addition to aliphatic saturated dicarboxylates, a number of substituted carboxylates (amino, keto, hydroxy) were also found to form double salts with OCP. One of the most important findings of this study is the formation of OCP-citrate double salt, since citrate is found in bone.

Studies of the crystal structure of a calcium phosphate pyrophosphate, $Ca_2KH_3(P_2O_7)_2 \cdot 3H_2O$, suggest a layer-type feature. The interlayer linkage of pyrophosphate ions and Ca ions indicates a possible mode of attachment of pyrophosphate on apatite surfaces that could interfere with crystal growth and/or dissolution.

The effects of magnesium and trace ions such as fluoride and lead on the hydrolysis of OCP were studied. Hydrolysis of OCP has two steps, nucleation and growth. Fluoride ions increased both nucleation and crystal growth. Magnesium ions decreased the nucleation but did not affect the growth rate. Lead was readily incorporation into the hydrolysis products. These studies show that the kinetics of OCP hydrolysis is significantly affected by the presence of trace ions.

DENTAL ALLOYS, CERAMICS, METROLOGY, AND ANALYSIS

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Work has continued on the use of the Weibull distribution for analyzing the fracture strength of adhesively bonded metal systems under differing test methods and geometries (ie. three-point and four-point bending and uniaxial tension with varying adhesive layer thickness). The test results indicate that the characteristic Weibull parameters are dependent on the type of test employed and the volume of the test sample. Uniaxial tensile tests have lower fracture strengths than bending tests. Beam theory stress analysis indicates that the probability of failure per unit volume is higher for thinner specimens, but not significantly so. Finite element modeling shows beam theory is inappropriate. Fractography shows failures often originate at the adhesive surface.

The Weibull parameters, were obtained for an experimental composite resin as a function of the filler-to-resin ratio (F/R). The filler-to-resin ratio varied from F/R = 1.5 to F/R = 5. The shape parameter of the distribution function did not change with the changes in the filler resin ratio.

Work was begun on the effect of silanization on the diametral tensile stress (DTS) of composite resins and the DTS value as a function of time in air (4 hr - 24 hr). Preliminary results have shown a significant amount of post cure occurs after 4 hrs (This is part of Dr. T. Matthews as visiting scientist).

The software for the positioners of the profilometer has been upgraded by the manufacturer eliminating most problems with the micropositioning stages and the programming of these positioners.

An algorithm has been developed to calculate a predicted service life for a dental prostheses when a limited number of clinical failure data are available and the survival times of the remaining prostheses span a range of times instead of a single termination time. This algorithm has been modified by the equations developed by Cohen to include withdrawals of non-failed specimens from the sample population. This is referred to as progressive censoring. No calibration of this software has yet been done. Tables by Harter and Moore have been identified as a source for possible "bench work" data.

Finite element modeling of porcelain fused-to-thin-metal strips shows that curvature is not highly sensitive to residual stresses developed from non-equilibrium cooling. The results cast serious doubts about the use of curvature as an indicator of thermo-mechanical stress compatibility.

OUTPUTS/INTERACTIONS

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Industrial and Academic Interactions

Industrial

Staff of the Polymers Division co-hosted a workshop with **SACMA**, the Suppliers of Advanced Composite Materials Association, to develop a program which will produce test methods for polymer composites which will have industry-wide acceptance. In attendance were representatives from DoT, SAE, ASTM, BASF, Hercules, and the DOD standardization effort. An action plan for speeding the development of standards was formulated.

Division scientists are working together with **duPont** to evaluate test methods for characterizing composite materials. When very thick parts are made with composites, variations in the material properties through the thickness can be an important problem. This program has identified 20 different test methods that have the potential for examining these differences.

A collaborative effort with the **National Center for Manufacturing Science** (NCMS) identifies critical problem areas in composite processing and formulates plans to address these problems. NCMS is a consortium of more than 85 U.S. companies with interests in the processing area.

Working with **Ferro Corp.**, Division scientists have developed a procedure to use cure monitoring techniques to optimize cure cycles for thermoset resins. This procedure was demonstrated with a commercial system from Ferro.

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.

A project sponsored by the **Electric Power Research Institute** (EPRI) to investigate space charge distributions in polyethylene and ionmers and its influence on electrical breakdown has been completed; the final report is in preparation. Two staff members participated in a 3-day EPRI workshop directed toward identifying areas of polymer research that would be of value in addressing problems of the electric power industry.

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. has initiated a new effort which makes proprietary use of the Polymers Division x-ray facilities to provide morphological data on polyester fibers as a function of spinning conditions.

Rohm and Haas Co. has initiated a new Industrial Research Associate agreement aimed at developing methods for using small-angle x-ray scattering to characterize the structure of dispersions of a variety of polymeric materials including micelle formers and copolymers with hollow centers.

A cooperative program with **Union Carbide** has been established in which our thermal pulse measurements of charge distribution in polymer films are being correlated with the resistance to water-tree formation in specially prepared polymer formulations.

Research Associate agreement with **Armstrong World Industries** may lead to a better understanding of long time flow properties of composite polymeric materials. The collaborative attempt will be made to determine the molecular basis of time and temperature variations in viscoelastic glass forming materials.

An agreement has been signed with **duPont** for characterization of molecular composites by solid state nuclear magnetic resonance spectroscopy. The materials are produced by duPont as part of an Air Force program to commercialize these novel materials.

Discussions are in progress with members of **ASTM-D20** subcommittee on thermal methods on the production of a polypropylene SRM for which the melt flow rate will be certified. This standard reference material will facilitate 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.

A program of technology transfer has been initiated with **E.I. duPont de Nemours Co.** to study copolymerization of, and possible applications for, functionally terminated poly(methyl methacrylate)s. DuPont has supplied custom made samples of these macromonomers for studies in the Polymers Division.

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

The Research Associate agreement with **Westinghouse** Research and Development Center to transfer measurement techniques for compliant piezoelectrics has been renewed.

Projects on polymer blends are planned with **Exxon, IBM, Eastman Kodak, Hercules, Mobil 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 **Institute of Paper Chemistry**, Appleton WI collaborates on measurements of the chemical and physical structure of cellulosic materials by infrared spectroscopy, x-ray diffraction, and solid state nuclear magnetic resonance spectroscopy.

A research associate agreement with **Dentsply International** was renewed. One accomplishment of the collaboration has been development of a near infrared method to study the absorption of water by dental resins and composites.

Numerous contacts with various segments of American industry have evolved regarding the sterilization process developed in the Polymers Division. A new cooperative research and development agreement for gas plasma sterilization was formalized in August with **Air Techniques, Inc.**

The **J. Morita Corporation**, and **Pentron Corporation** have supplied materials useful in conducting dental materials research.

A Research Associate agreement with **Technical Assessment Systems, Inc.** continues research to detect trace levels of organotin species by a laser bioassay system.

Industrial/Academic

A joint program between the Polymers Division, **Hi-Tek Polymers**, and the University of Massachusetts continues to explore the molecular network structure of thermoset resins used in composites. In recent studies, Division scientists have used model materials supplied by the university to examine the effects of molecular weight distribution in the starting resins, and a model commercial resins provided by Hi-Tek to extend the test to realistic materials. The joint Polymers Division-**Polaroid**-Kyoto Institute of Technology (KIT) project has continued to examine the structure of polyvinyl alcohol (PVA) gels that are the precursors to high strength fibers and films. Studies in the Polymers Division on special PVA materials provided by Polaroid and KIT have revealed important information about the changes that occur during gelation.

A series of electric cable insulations subjected to ac aging tests by **Detroit Edison** and partially characterized by researchers at the University of Connecticut have been subjected to charge distribution measurements in a cooperative effort.

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

Research involving the Chemical Engineering Department at Johns Hopkins University and supported by **EPRI** focusses on the bioprocessing of coal by hyperthermophilic bacteria. The is also investigating the forms of organic sulfur in coal. Progress in this area is helping pinpoint new coal processing options aimed at reducing emissions of sulfur to the environment.

A joint Polymers Division-**Gencorp**-University of Kyoto project will address microstructure and isotope effects in rubber/rubber blends. Miscibility and phase diagrams will be determined and mechanical blending/phase separating processes will be determined for immiscible rubber/rubber pairs. The desired information is particularly valuable to the rubber industry.

Academic

Dr. Naoto Tsutsumi of Kyoto Institute of Technology spent his year of sabbatical leave in the Polymers Division. While here, he initiated a program to use changes in optical absorption spectra of molecules dissolved in ferroelectric polymers to yield information about internal electric fields in the polymers. This work is related to our program in nonlinear optics.

Dr. Aime DeReggi of our staff was an Invited Professor at the Ecole Superieure de Physique et de Chimie Industrielles in Paris, France during April and May 1989. While there, he had an opportunity to compare our thermal pulse measurement of charge distribution with the complementary technique of laser-induced acoustic pulse generation.

Mr. Zicai Liang of Chengdu Institute of Technology, Peoples Republic of China is a foreign guest scientist in the Specialty Polymers Group for 13 months, beginning May, 1989. He is investigating the electric field orientation of vinylidene cyanide-vinyl acetate copolymer as a host for NLO molecules.

A cooperative program with Professor Barry Farmer of the University of Virginia explores by potential energy calculations the energy that might be stored in polymer chain folds as a result of orienting polar molecular stems in an electric field.

Professor Ray Chen at the University of Maryland, Baltimore County is cooperating with us in making measurements on the nonlinear optical properties of polymers prepared in our laboratories.

Dr. Richard P. Blakemore and his group at the University of New Hampshire is collaborating with Polymer Division scientists in the characterization of metal particle formation in bacteria by X-ray and neutron scattering techniques.

A collaborative program with Drexel University has been established to use optical probes based on fluorescence spectroscopy to monitor processing parameters during injection molding. A Drexel University student is learning this measurement technology by working in our laboratory.

Specimens prepared at Stevens Institute of Technology were evaluated for their fluorescence intensity distribution in conjunction with an ongoing program of cooperation between our laboratories to monitor and model the mixing and extrusion of highly filled polymers.

A joint program with Drs. Ron Eby and Herzl Chai of Johns Hopkins University investigated the use of adhesive joint fracture tests as a method to simulate, in a controlled way, interlaminar fracture in a composites. Johns Hopkins performed the fracture experiments while the Polymers Division supplied expertise in the analysis of deformation mechanisms in polymers. This work has produced a new fracture test with important advantages over current tests which are performed on composites.

A new joint program was initiated with Michigan State University to investigate test methods for fiber-matrix interface strength in composites. A variety of currently available measurement techniques will be used to evaluate model systems carefully prepared to have a variety of interface strengths. The test results as well as the advantages and disadvantages of each method will be compared to determine the current state-of-the-art in this field.

A number of projects involving polymer solution properties are being pursued in collaboration with Prof. Karl Freed of the University of Chicago. These projects include polymer adsorption with excluded volume interactions, the virial coefficients of polymer mixtures and the effect of many body interactions on solution properties such as the radius of gyration. The effect molecular architecture on solution properties is also being pursued.

Collaborative work is being pursued with Prof. Richard Gaylord of the University of Illinois on rubber elasticity and the swelling of rubber. Present work involves the testing of a molecular theory of rubber elasticity and the formulation of a theory for swelling.

A collaborative program is being carried out with Prof. D. E. Kranbuehl at the College of William and Mary on computer simulation studies of the dynamical behavior of polymer chains.

A doctoral candidate from the University of Maryland has used small-angle x-ray scattering to help devise methods for forming crystalline aggregates of ethylene glycol oligomers which will serve as model systems in studies aimed at characterizing the effects of irradiation on chain conformation and mobility in polyethylene oxides.

A doctoral candidate from the University of Delaware is using small-angle x-ray scattering to characterize morphological changes which occur when highly oriented polyester fibers are annealed at temperatures somewhat below their melting points.

Polymers Division staff have collaborated with a staff member from the University of Dayton to characterize the effects of compressive deformation on the microstructure of fibers from rigid rod polymers embedded in epoxy matrices. These materials are models for high-strength composite materials.

Collaboration with Professor Herve Marand, Virginia Polytechnic Institute, focusses on the morphology and crystallization behavior of polypivalolactone.

Professor Eric Amis, University of Southern California and Polymers Division staff are studying the morphology of solution grown polymer crystals through a new seeding technique.

Small angle neutron scattering studies of the effect of crosslinking on miscibility in rubber-rubber polymer blends are in collaboration with Professor T. Hashimoto of the Kyoto University in Japan.

Collaborative programs in the area of blends include work on single chain conformations and diffusion with the Universities of Wisconsin and Minnesota, and an ongoing NSF/JSPS-sponsored program on block copolymers in Microphase-separation systems with Nagoya University.

The Dental and Medical Materials Group participated with professors from the University of Florida in planning an August, 1989 conference on dental materials. A special symposium on measurement and analytic methods was co-sponsored with the Academy of Dental Materials. Several papers with researchers from Tokushima University, Japan on stress in porcelain-metal systems have been prepared/or published. One paper on casting of dental alloys has been coauthored with a research from Tokyo Medical and Dental University. Studies on the bonding of resins retained prosthetic systems was initiated with guest researchers from Hiroshima University and the University of Maryland. Investigations into the strength and durability of dental composites via the use of Weibull analysis were initiated with guest scientists from the University of Maryland and Howard University. A collaborative study with Loyola University on fluoride caries inhibition is underway. Guest Scientists from the Rudjer Boskovic (Yugoslavia) and Nihon University (Japan) have been working on calcium phosphate chemistry. Calcium phosphate cements are being developed cooperatively with scientists at Taiwan University. Collaborative work with a University of Maryland researcher is in progress on statistical methods to predict results of clinical studies in progress.

Associated Activities

Invited Talks

Division personnel presented a total of 124 invited talks on research activities at the following types of organizations and symposia: industrial laboratories, 19; international symposia, 9; universities, 38; topical symposia, 15; national and government laboratories, 20; professional society meetings, 17; and Gordon Conferences, 6.

SRMs and Patents

SRM 1487, a low molecular weight poly(methyl methacrylate), PMMA, certified for molecular weight by ultracentrifugation was issued. This completes the certification of the three PMMA standard reference materials. This work was supported by the Navy and OSRM.

A standard reference material for melt flow rate was certified. The polyethylene, SRM-1474, material with a melt flow rate of 5.03 g/10 min will be used to check equipment stipulated by the ASTM D-1238 voluntary standard.

A pyrite reference material was prepared as a bioleaching test standard. The material should be of use to academic and industrial laboratories evaluating microbial processing of coal and metal ores. The material will be used in connection with a Polymers Division-proposed standard test method for determining bioleaching rates of ores. This method is currently under review by ASTM E-48.03.

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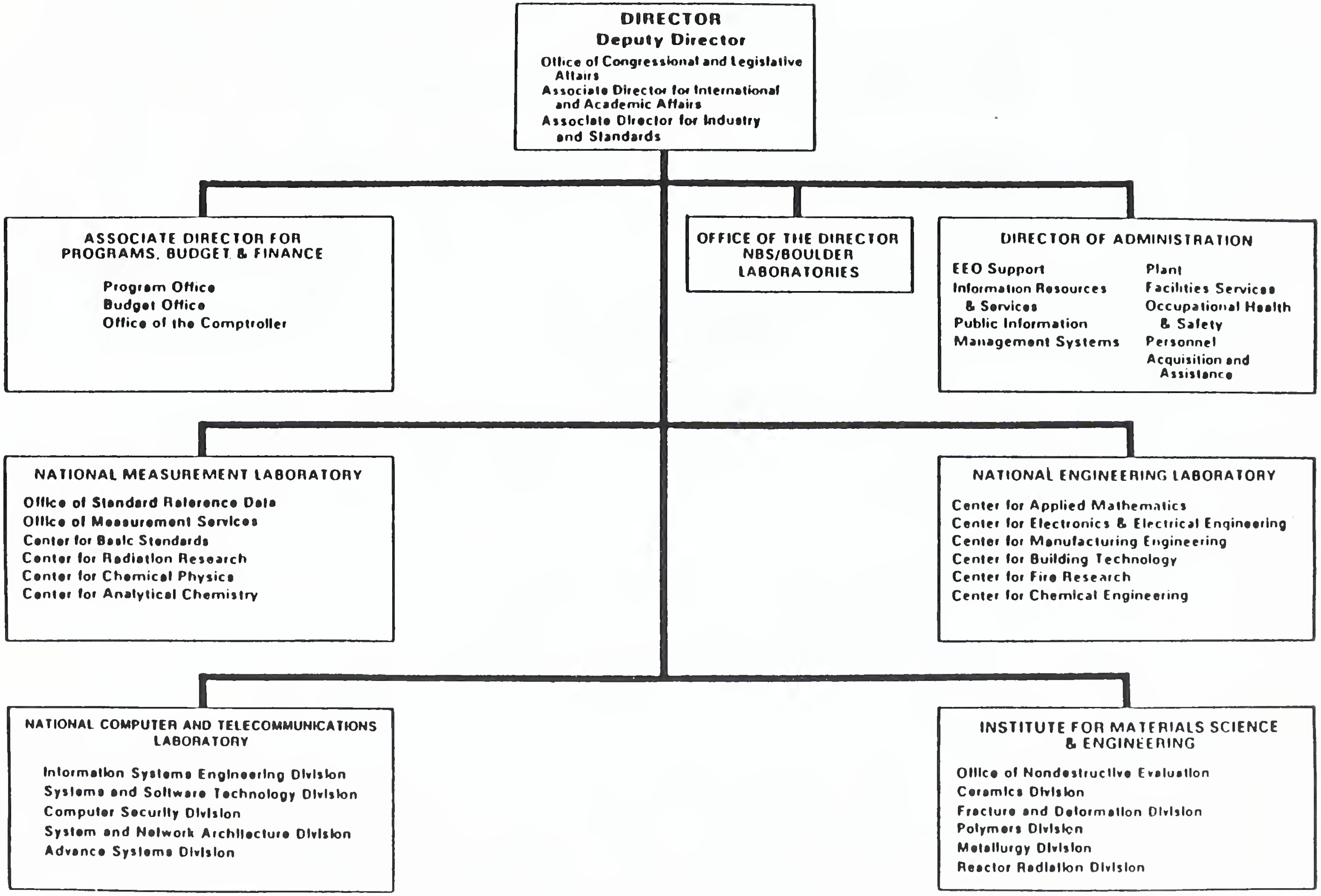

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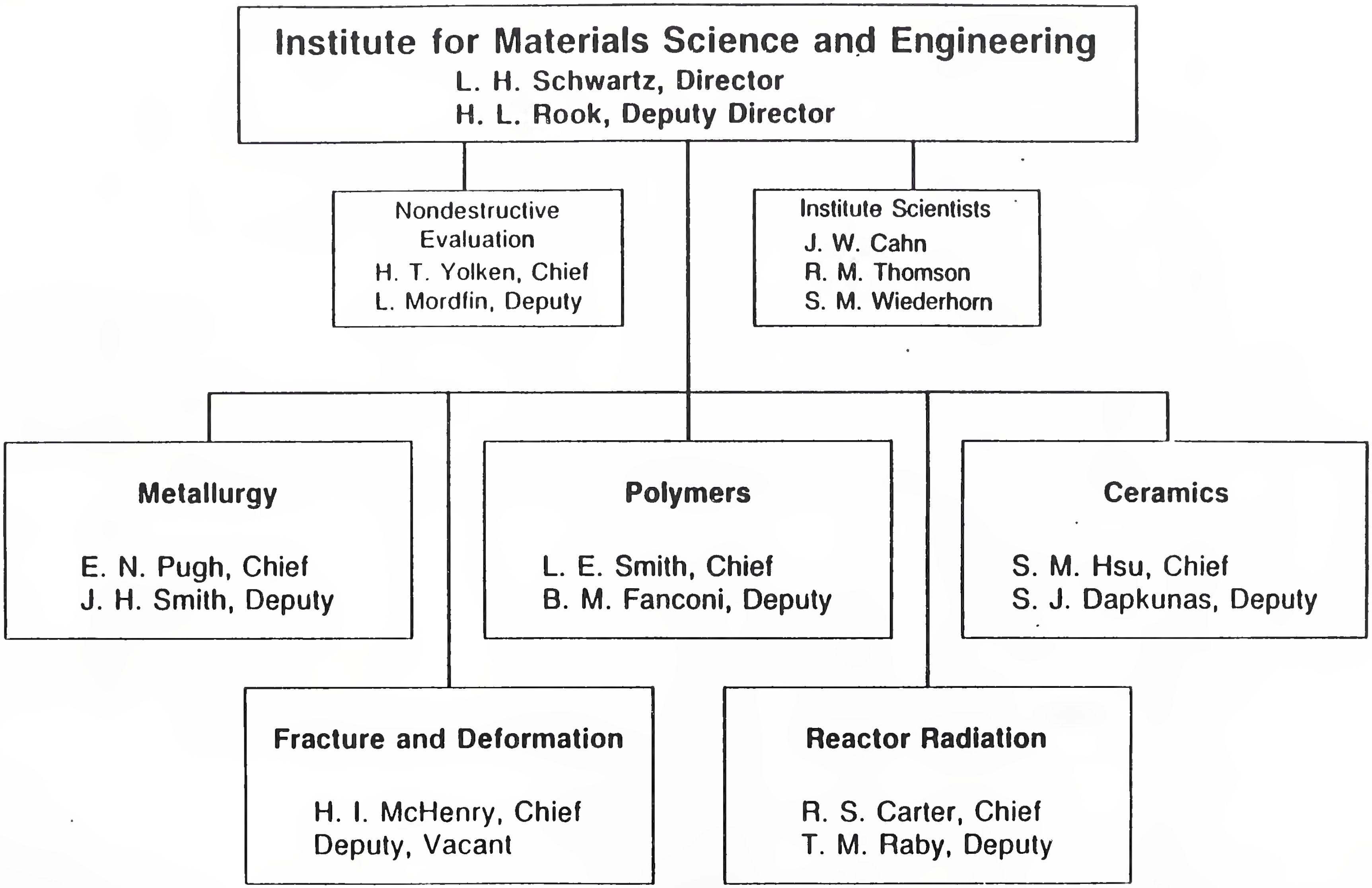
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