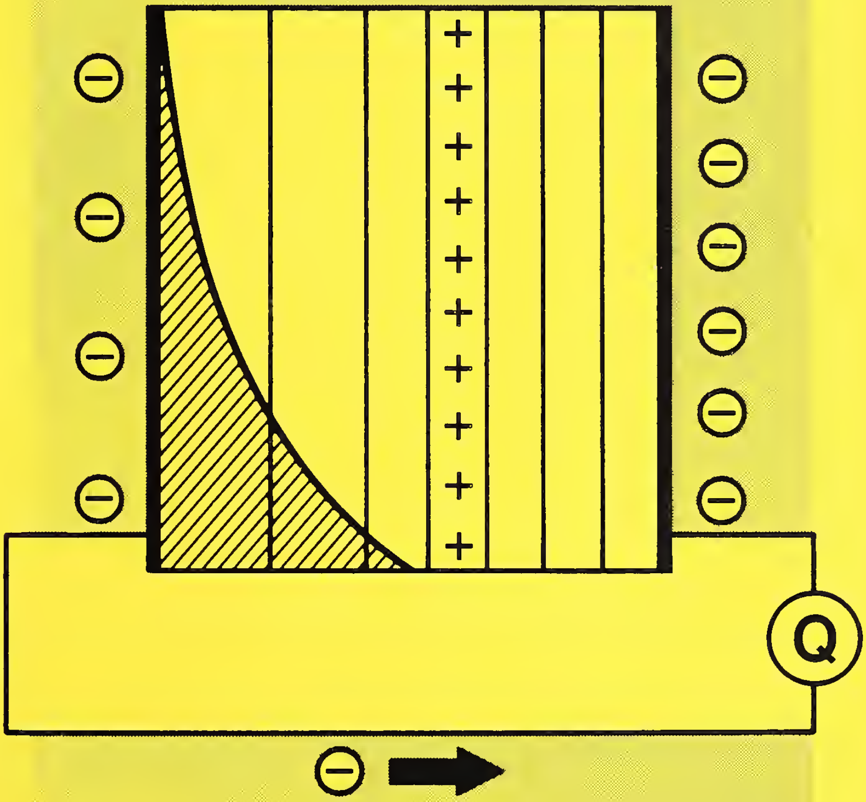
IMSE

Institute for Materials Science and Engineering

POLYMERS



NAS-NRC
Assessment Panel
January 21-22, 1988

NBSIR 87-3614
U.S. Department of Commerce
National Bureau of Standards

Technical Activities 1987

A schematic diagram of a laser-induced thermal pulse (hatched area), after entering the left side of a polymer film with imbedded positive charge. The non-uniform thermal expansion displaces the charge with respect to the electrodes and causes a current in the external circuit. The space charge distribution is determined from this current. The technique, developed at NBS, allows us to guide the electric power industry in ways to reduce the effects of charging of polymeric insulation used in power cables.

IMSE

Institute for Materials Science and Engineering

POLYMERS

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

NAS-NRC
Assessment Panel
January 21-22, 1988

NBSIR 87-3614
U.S. Department of Commerce
National Bureau of Standards

Technical Activities 1987

POLYMERS DIVISION

CHIEF

Leslie E. Smith
Phone: (301) 975-6762

DEPUTY CHIEF

Bruno M. Fanconi
Phone: (301) 975-6770

ASSISTANT CHIEF

Martin G. Broadhurst
Phone: (301) 975-6765

GROUP LEADERS

Electrical Properties
G. Thomas Davis
Phone: (301) 975-6725

Chemical Performance & Standards
Francis W. Wang
Phone: (301) 975-6726

Mechanical Performance
Bruno M. Fanconi
Phone: (301) 975-6770

Polymer Composites
Donald L. Hunston
Phone: (301) 975-6838

Polymer Blends
Charles C. Han
Phone: (301) 975-6771

Dental & Medical Materials
John A. Tesk
Phone: (301) 975-6801

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.

TABLE OF CONTENTS PAGE

INTRODUCTION

POLYMERS DIVISION

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

The Polymers Division is responsible for providing standards, measurements, and fundamental concepts of polymer science to assist U.S. industries that produce, process, or use synthetic polymers as an essential part of their business. In order to focus this broad mission on specific technical programs, we look for trends in the industries concerned and try to anticipate future needs. The programs of the Division which are described in this report are the result of such past planning. For example, work done by Division scientists on the fundamental science underlying phase separation in polymer blends is the result of many interactions with the industrial and scientific community, including a comprehensive workshop to identify the critical unmet needs of the industry. Focus on polymer blends in general is a recognition that these materials are growing rapidly in use and may well become the commodity polymers of the next decade in the U.S.

Polymer matrix composites show similar promise of rapid growth and widespread application in many industries. Polymer composites are already indispensable in many military and aerospace products but the potential impact of these materials on high volume commercial markets is impressive. In the next ten years, advanced composites are predicted to have an annual value of over $10 billion and the automotive industry may be the largest single user of composites. For these forecasts to be fulfilled, we must learn to process composites inexpensively and reliably as well as understand the long term durability of these materials in service. We are developing a program plan to address these issues and will begin implementation during FY 88. This report contains descriptions of technical projects that will become important parts of a more comprehensive program next year.

There are many opportunities for innovation and cost savings that could be realized through more intelligent design and control of processing. Industry trends already reflect a need for more research on the fundamental principles involved in the processing of polymers. We have begun to study some applications of novel sensors for viscosity, flow, and mixing that are the beginning of an increased emphasis on providing this science base.

One of the ways in which we provide technical services to industry and the scientific community is by making major measurement facilities available for collaborative research or, in some cases, for proprietary measurements. This past year we have opened up our 10-meter small angle x-ray scattering facility to outside users. These users have been interested in the structure of novel blend systems, the structure of high strength fibers, and measurement of structure in processed sheet and film. The facility is useful in measuring structures on a size scale in the 1- to 100 nanometer range. We welcome inquires from any other potential users.

The range of Division programs is described in this report, organized according to these six Groups:

ELECTRICAL PROPERTIES
CHEMICAL PERFORMANCE AND STANDARDS
MECHANICAL PERFORMANCE
POLYMER COMPOSITES
POLYMER BLENDS
DENTAL AND MEDICAL MATERIALS

These Groups have made a number of significant accomplishments during the last year. Some of these are summarized below with references to the section of the report where more information about the work may be found.

- A non-destructive measurement technique for determining the total charge trapped within a polymer film has been devised to complement our ability to determine the spatial distribution of the charge. Experiments with polyethylene, zinc ionomers of polyethylene-methacrylic acid copolymers, and blends of the two all show nearly uniform distribution of negative charge after charging to steady state conditions with an applied electric field (pg. 4).

- A series of new diacetylene monomers designed to yield polymers exhibiting large non-linear optical coefficients have been synthesized. Anticipated liquid crystalline phase behavior has been realized in one of the monomers. Many of the others are expected to yield liquid crystalline structures when polymerized (pg. 7).

- A patent was awarded to the U. S. Government for the use of interpenetrating networks as solid electrolytes. This material combines low molecular weight poly(ethylene oxide), a cured epoxy resin and dissolved salts. The salts apparently provide mobile cross-links that keep the normally liquid PEO from phase separating (pg. 81).

- Two polyurethane Standard Reference Materials are being produced with support from the Food and Drug Administration and the Office of Standard Reference Materials. These SRM's with certified values of weight-average molecular weight will help meet a growing need for better methods of characterizing polyurethane used in medical devices, both before use and after degradation following implantation (pg. 10).

- Two linear low density polyethylenes used in gas piping (one with, and the other without pigment) have been characterized for certification as Standard Reference Materials, with support from the Gas Research Institute and the Office of Standard Reference Materials. Such standards will be useful not only to the gas distribution and associated industries but also to the rest of the scientific community. For the pigmented resin, a certificate has been issued certifying the melt flow rate (pg. 12).

- A Research Associate Program has been initiated in collaboration with AT&T Bell Laboratories to develop a fluorescence technique for monitoring the formation of polyimide polymers. The program aims to measure changes in fluorescence spectra occurring during the formation of polyimide polymers from poly(amide-acid) precursors. These changes can be measured in-situ and non-destructively to monitor the course of imidization (pg. 17).

- A new class of polymeric resins has been designed and synthesized as candidates for electron beam curable inks. These materials show very good drying behavior, viscosity, and water washability prior to cure. The latter property is essential for success in water-wipe intaglio printing. On-line printing experiments are currently underway at the irradiation facility at BEP (pg. 39).

- A percolation model was successfully applied to a theory of network formation in thermosetting composite resins where crosslinking reactions are not dominated by linear polymerization reactions. Neutron scattering and computer modeling results confirmed applicability of the theory (pg. 41,42).

- A model was developed for large strain deformations in thermosetting polymers. Small angle neutron scattering experiments showed little change in the average distances between crosslinks as a sample was deformed. This result indicates that the strain is accommodated via inter-chain rather than intra-chain deformation, and suggests a network unfolding mechanism (pg. 43).

- A new adhesive which adheres to both hard and soft tissues was formulated. Its basic component is an acrylic backbone with pendent isocyanate groups. The new adhesive was shown to produce bonds equivalent in strength to bone (pg. 62).

- The use of α-methylene-C-butyrolactone in polymerizable dental resins was found to enhance the degree of cure of the hardened polymer. This and other advantages make this monomer a potential replacement for methyl methacrylate in dental composites, denture bases, bone-cements and related biomedical applications (pg. 56).

- The Cahn-Hilliard-Cook equation has for the first time been proven to be quantitatively correct. The equation was applied to spinodal decomposition of a polystyrene/poly(vinylmethylether) blend system. Data verifying its accuracy came from time resolved temperature jump and reverse quench light scattering techniques, and from a structure factor measured by a SANS experiment (pg. 50).

- The mutualdiffusion coefficient, D, of a polymer blend was shown to be a continuous function of temperature at and around a compatible-incompatible phase boundary. The value of D, which changes sign at the boundary, leads to derived mobilities that have an Arrhenius temperature dependence (pg. 50).

- A single phase interpenetrating network was formed from linear poly(vinylmethylether). Such single phase interpenetrating networks are rare because the normal statistical spatial variations in numbers of crosslinks usually cause phase separation (pg. 51).

- Entropy theory was successfully applied to glass formation in polymeric ring systems. The glass formation temperatures increase sharply with decrease in molecular weight for these ring polymers, while the opposite is true for the much more common linear polymers. The theory was shown to predict both results (pg. 62, Ref.).

- Current published models of the gel structure in isotactic polystyrene/decalin gels were corrected and refined with NMR data. High decalin mobility precludes the possibility of a polymer/solvent complex. Relatively high polymer mobility is indicative of small gel particle size and plasticization of the styrene by the decalin (pg. 30).

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
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
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
Carey, Clifton M.*	o Dental plaque o Microanalytical analysis techniques
Chang, Shu Sing	o Thermal properties of polymeric and composite materials o Electronic packaging o Polymer phase transitions o Precision electrical and temperature measurements

*Research Associate

Chow, Laurence C.*	o Calcium phosphate compounds o Dental and biomedical cements o Solution chemistry o Topical dental fluorides
Crissman, John M.	o Mechanical behavior o Environmental stress-cracking o Failure and fracture of polymers
Davis, G. Thomas	o Piezoelectricity in polymers o Polymer crystallization o X-ray diffraction of polymers o Ionic conduction in polymers
Dehl, Ronald E.	o Surface analysis o Remote fiber fluorescence o Ellipsometry o Bonding of polymers & composites
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
Dickens, Brian	o Kinetics of thermal degradation of polymers o Photodegradation of poly (methyl methacrylate) o Curing of thermosetting resins including printing inks
Di Marzio, Edmund A.	o Statistical mechanics of polymers o Phase transitions o Glasses o Polymers at interfaces
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

*Research Associate

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
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 Polymer blends o Polymer characterization o Small angle neutron scattering o Static and quasi-elastic light scattering
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 composites o Flow behavior of dilute high polymer solutions o Macromolecule-small molecule binding
Johnston, Allen, D.*	o Nuclear magnetic resonance o Mossbauer studies o Chemical adhesion

*Research Associate

Khoury, Freddy A.	o Crystallization, structure and morphology of polymers (including polymer blends) o Analytical electron microscopy of polymers o Wide angle and small angle x-ray diffraction o Structure and mechanical property relationships
Kirkpatrick, Diana M.*	o Adhesion o Chemical analysis
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
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
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

*Research Associate

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
Passaglia, Elio	o Fracture and crazing o Linear viscoelasticity o Crystallization theory
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
Rupp, Nelson W.*	o Clinical dentistry o Amalgams o Direct golds o Dental standards o Composites o Titanium castings o Microleakage o Dentin adhesives
Schen, Michael A.	o Living polymer synthesis o Polymers for non-linear optics o Molecular electronics
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
Stansbury, Jeffrey W.	o Synthetic chemistry o Polymers and polymer composites o Polymerization expanding monomers
Takagi, Shozo*	o Crystallography o X-ray diffraction o Calcium phosphate compounds

*Research Associate

Tesk, John A.	o Casting of alloys o Strength of dental systems o Thermal expansion & properties of dental materials o Finite element studies o Porcelain-metal system
Tomazic, Branko*	o Atherosclerotic plaque o Biological calcium phosphate compounds
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
Venz, Sabine*	o Clinical dentistry o Dental composites o Dental polymers
Verdier, Peter, H.	o Polymer solution properties o Polymer chain dynamics in solution o Statistical analysis of data o Error estimation o Computer simulation of polymer chain dynamics
Vogel, Gerald L.*	o Dental plaque, biological solution chemistry of calcium phosphates o 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

*Research Associate

Zapas, Louis J.	o Continuum mechanics & Rheology o Non-linear mechanical behavior of polymers o Static fatigue of plastics o Finite elasticity (rubbers)

ELECTRICAL PROPERTIES

The goal of the task on electrical properties is to carry out long-range research involving the interaction of electric fields with polymers. Our results provide the basis for new or improved measurements which will lead to higher performance of polymers in existing applications or to entirely new applications. Examples of the interaction of electric fields with polymers which are investigated in our program include measurement of dielectric constant and loss, determination of charge or polarization distribution in films, development and application of piezoelectricity and pyroelectricity in polymers, ionic conduction in solid polymers, and electro-optic measurements on specially synthesized materials.

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 NBS 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. Also, an automated system which measures dielectric constant and loss at a series of fixed frequencies between 100 Hz and 10^9 Hz is being used to infer DC conductivity of polymer systems where polarization becomes a problem.

The recently improved sensitivity and resolution of our laser-induced thermal pulse technique for measuring charge and polarization distribution in thin polymer films is extremely useful in a variety of programs. Measurement of trapped charge and its effect on altering applied electric fields in DC cable insulation has been studied; the distribution of charge in polymer films used in space applications is being investigated, and polarization distributions in multiple layered structures of vinylidene fluoride - trifluoroethylene copolymers of different composition have been measured.

Experience and knowledge gained from our research into piezoelectric and pyroelectric polymers continues to be applied to the development of transducers for other agency needs. We are also frequently called upon for technical information in this area by companies interested in developing applications for these polymers. A great deal of commercial interest has also been shown in our development of an ion-conducting interpenetrating polymer network consisting of low molecular weight polyethylene oxide and epoxy resin. Studies of $^6Li^+$ diffusion in solid polymers using neutron depth profiling are continuing.

A relatively new effort in the Electrical Properties Group involves the synthesis of monomers and polymers designed to exhibit large non-linear optical coefficients. The research 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 non-linear 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.

FY 87 Significant Accomplishments

- A non-destructive measurement technique for determining the total charge trapped within a polymer film has been devised to complement our ability to determine the spatial distribution of the charge. Experiments with polyethylene, zinc ionomers of polyethylene-methacrylic acid copolymers, and blends of the two all show nearly uniform distribution of negative charge after charging to steady state conditions with an applied electric field.

- A series of new diacetylene monomers designed to yield polymers exhibiting large non-linear optical coefficients have been synthesized. Anticipated liquid crystalline phase behavior has been realized in one of the monomers. Many of the others are expected to yield liquid crystalline structures when polymerized.

- A patent was awarded to the U. S. Government for the use of interpenetrating networks as solid electrolytes. This material combines low molecular weight poly(ethylene oxide), a cured epoxy resin and dissolved salts. The salts apparently provide mobile cross-links that keep the normally liquid PEO from phase separating.

- Time-evolution of dielectric spectra in a curing epoxy resin have been successfully correlated with ultrasonic attenuation, shear viscosity, heats of reaction, and fluorescence measurements. Dielectric measurements using the time domain spectrometer continue to be a promising technique for cure-monitoring in composites.

Automated Dielectric Measurements

F. I. Mopsik

The development of a time-domain spectrometer has begun to attract increasing attention as awareness of its capabilities has spread. The instrument measures the charge response of a dielectric to an applied voltage step for times from 10 μs to 3000 s. The data is then transformed to measurement accuracy into the equivalent frequency range of 10 kHz to 0.0001 Hz. A commercial version of the instrument is being developed by IMASS, Inc., Hingham, MA through the Research Associate program at NBS and the first prototype has been assembled and tested for operation.

The instrument's sensitivity, accuracy and wide frequency range allow relaxation studies that would be difficult by any other means. Guests from Alcoa and Johns Hopkins University have visited NBS to see if dielectric measurements would be useful for checking for compatibility of blends and the possible plasticization of membranes by gases at high pressure.

Process Monitoring of Composite Resins

Following the work on epoxy cured with imidazole, a systematic study was made on a system cured with a diamine. Cross comparisons were made with ultrasonic attenuation, shear viscosity, thermal evolution and two forms of fluorescence measurement that measure the rotational behavior of a probe and self-diffusion.

The dielectric data at 45 °C show a pronounced minimum followed by a maximum in 50 Hz conductance during cure. Loss spectra taken just after the conductance maximum show the presence of a dipolar relaxation that evolves towards longer relaxation times as the cure progresses. This relaxation can be associated with a glass transition but the time scales involved are such that a complete relaxation curve can never be achieved. Also, the data allowed the monitoring of the limiting DC conductivity as the cure evolved well past the gel point. This data showed that electrical measurements can be used to follow system evolution well past gelation. There was good correlation with other techniques within mutual experimental limitations, although, viscosity again changes much more quickly and becomes unmeasurable early in the cure.

In the area of fiber reinforced polymer composites there is a great deal of interest in using thermoplastic resins with high T_g in place of the irreversible thermosetting resins such as the epoxies. The processing of such composites requires heating to high temperatures where the resin will flow under pressure and then cooling. One of the most promising thermoplastics for such applications is polyether ether ketone (PEEK) which is a semi-crystalline polymer. The properties of the composite depend upon the degree of crystallinity in the polymer matrix which in turn depends upon the thermal history. Molecular motions responsible for dielectric loss are expected to be different in the liquid and crystalline phases, so the use of dielectric spectra to correlate with crystallinity changes during processing is being explored. Samples with very different thermal histories were examined between room temperature and 120 °C, a temperature range below T_g where no further changes are expected to occur. Small but easily observable differences between the samples were recorded but, in both cases, the major relaxation shifted outside the frequency range of the spectrometer at temperatures approaching 120 °C. Research in this area of commercial importance is continuing.

Reactor Cable Insulation Testing

In collaboration with the Electrotechnology Division under a contract with DOE, consultation services have been provided to evaluate test methods for use in estimating the life-time of cables used in reactor confinement. Since dielectric loss can be a monitor of the state of a dielectric, the use of the time-domain dielectric spectrometer and related techniques has been suggested.

As part of the program, some aged cable sections have been measured to demonstrate the utility of the method. In particular, three 30 cm long pieces of coaxial cable from the Shippingport reactor were measured at frequencies from 10^4 Hz to 10^{-2} Hz. One piece was from inside the confinement and two others were of the same temporal age, but had not been subjected to radiation. Both of the pieces that were not exposed to radiation were similar although small differences in the loss spectra could be seen. However, the sample exposed to radiation had a clear, radiation-induced conductance that was 100 times as large as the dielectric loss at 10^{-2} Hz at 50 °C. It should be noted that only at frequencies below 1 Hz could this effect be seen, illustrating the need for a wide frequency range especially low frequency to observe changes in material properties.

Thermal Pulse Measurement of Space Charge

A. S. DeReggi and M. G. Broadhurst

Space charge has been proposed as a possible cause of lowered breakdown strength of solid insulation by making local electric fields bigger than the applied field. One extensive study of this phenomenon, by researchers with the Electric Power Industry in Japan, led to a proposal to blend cross-linked polyethylene (XLPE) insulation with an ionomer to reduce space charge build-up. The authors used contact electrification (no applied field) as a measure of the tendency for a polymer to charge under an applied field and found that the XLPE acquired negative charge, the ionomer positive charge and a blend of the two acquired much less net charge than either component. The reverse-polarity breakdown strength of the blend was found to be higher than that of XLPE and this was related to its reduced contact charging. We have extended this work to test the above ideas and proposal for improving the performance of XLPE-insulated cables. In our study we measured electric field distributions in films of polyethylene, ionomers and blends charged by applying an electric field at temperatures between 20 and 80 °C for various times. These electric field measurements show more directly, than do contact charging data, the charging behavior that occurs in the bulk of coaxial DC power cable insulation in service under an applied field.

As part of the project, we made significant progress in analyzing and interpreting electrical transients induced by imbedded space charge when the surface of a dielectric polymer film is heated with short thermal pulses. We replaced the flash lamp light-pulse source with a dye laser to reduce the pulse duration to 1 μs, and improved the triggering circuit to obtain better than 1 μs data resolution. Measurement of the transient with and without a potential difference applied to the film allows 1) scaling and combining the transients obtained by heating each side of the film and 2) quantifying the resulting Fourier coefficients of the electric field distribution due to the imbedded space charge. This calibration procedure is all electrical, and does not require a knowledge of the energy in the pulse, the electrode absorbtivity, or thermal properties of the polymer film. We also showed that the response transient immediately after the thermal pulse involves the total charge and its first moment, so that by forming linear combinations of transient pairs (one for the thermal pulse applied to one of the electrodes and one for the pulse applied to the other electrode) the total charge and charge centroid in the polymer can be obtained from the transients without deconvoluting the data.

Electric field distributions in films of polyethylene and zinc ionomers of polyethylene methacrylic acid copolymers were measured with the improved thermal pulse method. Charging variables included applied fields from 0 to 50 V/μm, temperatures from 20 to 80 °C, times up to 1 week, and electrode metal. Initial differences in the signs and distributions of charge between nominally similar films were related to differences in the mechanical and thermal histories. At long charging times all films approached a steady state - nearly uniform distribution of negative charge. In this state the field due to the space charge was found to be a significant fraction of the applied charging field. The results were shown to be compatible with a model of homopolar injection of negative charge at the cathode and conduction of the injected charge through the film.

Conclusions from the work were:

1. Polyethylene, ionomers, and blends of the two materials accumulate a negative space charge after they are charged to quasi steady-state under a variety of conditions. The charge is distributed nearly uniformly throughout the bulk of the material. At 60 °C, steady state was achieved after about 1 hour.

2. The bulk space charge produces a field at the electrodes that is a large fraction of the applied charging field. For the small charging fields used in this study (relative to breakdown fields), the space charge field remained a small fraction of the breakdown field in all specimens.

3. There is generally no compensation of this negative space charge in the bulk by combining polyethylene with ionomers as suggested by contact electrification data.

4. In the sodium ionomers, enough positive space charge was detected within about 1 μm of the electrodes, to cancel some of the field due to negative space charge in the bulk of the films. The importance of this unresolved charge must be further investigated.

5. These results do not support the proposal that blending ionomers with XLPE insulation will generally improve the performance of coaxial DC power cables.

Two manuscripts describing this work have been submitted for publication in the proceedings of the 1987 IEEE Conference on Electrical Insulation and Dielectric Phenomena. The work was supported by the Electric Power Research Institute and was conducted along with a sister project at the University of Connecticut, to measure thermally stimulated currents from the same polymers described above.

Piezoelectric Polymers

A. J. Bur and S. C. Roth

Of critical importance in the study of energetic materials is the ability to measure the pressure of the high frequency shock wave generated during a fast burn or detonation. Unfortunately, no commercial technology is available which can supply a shock pressure gauge with the required low inertial mass and fast rise time. In an effort to develop such a gauge, the Naval Surface Weapons Laboratory in cooperation with Sandia Laboratories is funding research at the National Bureau of Standards to explore the application of piezoelectric polymers.

Because the pressures involved are much greater than those for which the physical properties of the polymer are linear and because the gauge is destroyed during the actual measurement, it is not possible to calibrate a gauge under actual conditions. Therefore a theoretical calibration curve of response versus pressure is used based on some physical characterization of the polymer gauge. The polymer film is made active by a molecular reorientation under the influence of an applied large electric field. If the field is applied as a slowly varying sinusoid (0.05 Hz) and the current through the polymer is recorded as a function of the electric field, a hysteresis plot is obtained. Subtracting out the components of the current due to the resistive and capacitive nature of the polymer sample yields the polarization current. Integrating the polarization current with respect to time produces the polarization charge. The charge at zero field is the remnant polarization of the gauge.

During the past year a semi-automated measurement technique to measure the remnant polarization has been developed. Using a specially developed electrode pattern, gauges which should have a rise time of several nanoseconds have been delivered to the Naval Surface Weapons Laboratory. These gauges will be used to study shock waves generated during high velocity impacts. Since the remnant polarization of the gauges is used to determine sensitivity, continuing research is being performed in an effort to better understand how differing processing parameters affect the remnant polarization.

Diffusion of $^6Li^+$ in Polyethylene oxide

C. K. Chiang and G. T. Davis

In collaboration with personnel from the Center for Analytical Chemistry at the NBS reactor, we are using neutron depth profiling to measure concentration profiles of $^6Li^+$ in polyethylene oxide from which we can deduce the diffusion coefficient of the salt in the polymer. Experiments have been performed in which we measured lithium concentration as a function of time in an initially salt-free film of PEO in contact with a thick film of PEO containing 10 mole% $LiC\ell O_4$ (7.5% natural abundance ^6Li). In this case, the concentration profiles were nearly flat and we used the total concentration as a function of time to obtain a diffusion coefficient on the order of 10^{-9} cm^2/sec at 25 °C. When the Li^+ was deposited as a thin film of $LiCF_3SO_3$ in low molecular weight polyethylene glycol on the surface of salt-free polyethylene oxide, we were able to deduce concentration profiles up to about 12 μm in depth which changed with time at 40 °C in a manner to be expected. From these profiles, we deduce a diffusion coefficient on the order of 2×10^{-10} cm^2/sec. Since the dissolved ions tend to cross-link the PEO and increase the T_g, the diffusion coefficient is expected to depend upon the concentration of salt in the polymer. We are now preparing samples using lithium salts which have been enriched with ^6Li to study isotope exchange rates in PEO-salt systems which have controlled concentrations of salt.

New Diacetylene Monomers and Polymers for Non-linear Optics

M. A. Schen

Within recent years, small organic molecules and polymer systems incorporating delocalized pi-conjugation have received much attention because of their unique electronic characteristics. A principal manifestation of this trend within the organic polymer community has been the rapid explosion of experimental and theoretical works in electrically conducting polyacetylene, polyaniline, and polypyrrole to name a few. Indeed, static dc conductivity measurements and magnetic susceptibility experiments identify these materials after n or p-type doping to be true synthetic metals. More recently, organic semiconductors and polymer semiconductors are being studied for their transient responses to high electric field strengths such as are associated with pulsed laser systems. Of these materials, the polydiacetylene family of polymers has received greatest attention for third-order non-linear optical processes.

The scope of this work involves the research into and ultimate exploitation of a unique aspect of diacetylene polymerization chemistry, i.e. the necessity of specific monomer organization for the conversion of monomer to polymer using thermal, UV, X-ray or gamma ray initiation. Traditionally this has been achieved by initiating polymerization within the monomer single crystal in the case of symmetric diacetylenes or in an organized molecular monolayer when working with amphoteric structures. Comparable experiments within an isotropic solution or melt of the monomer will not lead to high polymer. For many existing materials, dissipation of induced stresses developed as a result of polymerization results in catastrophic crystal failure giving rise to crystal defects or fibrillation. Optical losses in such structures combined with the limited material formats constitute major technological barriers to the commercial fabrication of integrated optical devices based on diacetylene polymers.

In an attempt to expand our understanding of the limits which geometric constraints have on diacetylene polymerization chemistry and physics and in the hope of overcoming existing material formatting limitations, two new classes of diacetylene monomers have been synthesized:

- **Class A**: monomers which exhibit liquid crystalline phase behavior and are expected to result principally in insoluble polymer.

- **Class B**: monomers which may or may not exhibit liquid crystalline behavior in the monomeric state but upon polymerization, are expected to yield side-chain liquid crystalline polymer architectures.

Within Class A monomers, 1-OBOA(1,6-bis[N-[4-oxybenzylidene] 4-n-octylaniline] 2,4-hexadiyene) is the one we have studied most. Through DSC and optical microscopy, mesophasic structures are observed over a 40° temperature range with both smectic and nematic structures tentatively identified. Thermal annealing within the liquid crystalline phase region shows also the slow evolution of lightly colored mesophase to a dark orange, non-birefringent phase which upon cooling forms a glass. After annealing at 180 °C, no thermal transitions are observed on subsequent cooling and heating from -40°C through

180 °C. Experiments are currently underway to determine the extent of polymerization in this sample and to examine the effect of UV, gamma or X-ray irradiation on 1-OBOA within the condensed phase and mesophase.

Within Class B monomers, a number of compounds have been successfully synthesized and are currently being examined. These include 4-COB(1,12-bis[4-cyano 4'-oxybiphenyl] 5,7-dodecadiyne), 4-CBOA(1,12-bis[N-[4-cyanobenzylidene] 4-oxyaniline] 5,7-dodecadiyne), and 4-OBOA(1,12-bis[N-[4-oxybenzylidene] 4-n-octylaniline] 5,7-dodecadiyne). In the condensed phase, none exhibit spontaneous polymerization at room temperature but do show varying degrees of polymerization with UV irradiation as evidenced by dark color formation and an invariance in the infra-red spectra. Controlled UV and gamma radiation initiated polymerization studies are currently in progress. By TGA, all monomers are thermally stable until at least 250 °C.

POLYMER STANDARDS AND CHEMICAL PERFORMANCE

The objective of this task is to provide to the polymer industry standard reference materials (SRM's) as well as measurement methods and data for predicting the lifetimes of polymers used in high volume or critical applications.

Polymeric SRM's certified for molecular weight are needed by the polymer industry to calibrate gel permeation chromatographs (GPC's) which are used routinely to measure polymer molecular weights and molecular weight distributions. The latter are the most important physical properties in determining a polymer's processibility and its end-use properties.

Improved techniques for polymer characterization and better understanding of polymer solution properties are essential to the efficient production of polymeric SRM's. Consequently, experimental and theoretical studies of polymer-solution properties are actively pursued in this task.

The most promising areas of growth in polymer markets are in construction, transportation, and electrical systems where long-term durability is essential. Enhanced durability requires a better understanding of the mechanisms by which polymeric materials are degraded because of environmental and other imposed stresses. In fact, a recent National Research Council report states, "Mechanistic data on degradation are essential (1) in identifying possible stabilization processes to slow degradation, and (2) in developing short-term methodologies for predicting service life."

Protective additives are needed for fabrication and long-term use of most polymers. In use, these additives inevitably diffuse through the polymer to some extent and may migrate out of the polymer entirely. The polymer is then left with poorer properties or made more vulnerable to degradation and failure. This is a major failure mode of polymers, and lifetime prediction methods explicitly include the rates of additive diffusion along with the rates of the inhibited and uninhibited degradation reactions. The number of commercially usable polymer-additive combinations is too large to be considered efficiently on a case-by-case basis. The emphasis in this task is, therefore, on the development of general principles or models of diffusion that are applicable to the widest range of generically important systems. In addition, knowledge of the general principles which control diffusion through solid polymers is important to the design and evaluation of improved additive systems.

FY 87 Significant Accomplishments

- A polymer processing program has been initiated to monitor polymer processing parameters by fluorescence spectroscopy. The ultimate goal of the program is to use fluorescence spectroscopy as an on-line nondestructive probe for real-time monitoring of processing parameters. Experiments have been carried out to demonstrate the feasibility of monitoring temperature, viscosity, and uniformity of mixing.

- Two polyurethane Standard Reference Materials are being produced with support from the Food and Drug Administration and the Office of Standard Reference Materials. These SRM's, with certified values of weight-average molecular weight, will help meet a growing need for better methods of characterizing polyurethane used in medical devices, both before use and after degradation following implantation.

- A series of three poly(methyl methacrylate) Standard Reference Materials are being produced with support from the Navy and the Office of Standard Reference Materials. These SRM's will be used for quality control of antifouling paints and as calibrating materials for the analysis of acrylic polymers. For SRM 1489 and SRM 1488, the polymers with the highest and the intermediate molecular weights in the series, certificates have been issued certifying both the limiting viscosity number and the number-average molecular weight.

- Two linear low density polyethylenes used in gas piping (one with, and the other without pigment) have been characterized for certification as Standard Reference Materials, with support from the Gas Research Institute and the Office of Standard Reference Materials. Such standards will be useful not only to the gas distribution and associated industries but also to the rest of the scientific community. For the pigmented resin, a certificate has been issued certifying the melt flow rate.

- A Research Associate Program has been initiated in collaboration with AT&T Bell Laboratories to develop a fluorescence technique for monitoring the formation of polyimide polymers. The program aims to measure changes in fluorescence spectra occurring during the formation of polyimide polymers from poly(amide-acid) precursors. These changes can be measured in-situ and non-destructively to monitor the course of imidization.

Standard Reference Materials

F. W. Wang, C. M. Guttman, P. H. Verdier, and J. R. Maurey

Work in this subtask concerns the production of polymer standard reference materials. The linear low density polyethylene standards currently under development, which are partly supported by the Gas Research Institute, will aid in the development of polyethylene gas pipes with improved properties. The poly(methyl methacrylate) standards currently in production will aid the Navy, which is partially supporting their production, in the development of long-lived antifouling paints for ships' hulls. In addition, both kinds of standards will be generally useful in the plastics and related industries, both for equipment calibration and as materials for research. Development of a self-calibrating gel permeating chromatograph should eventually result in a substantial reduction in the cost of producing polymer Standard Reference Materials, and should allow much more detailed characterization of polymeric materials than has thus far been practical.

Development of Polyurethane Characterization Techniques and Standards

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

During the coming year, we expect to produce these two polyurethane SRM's 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. The SRM's will not be the usual commercial polyurethanes, but rather will be model compounds to which the usual techniques for determining molecular weights of homopolymers can be applied. We also expect to develop methods for estimating compositional variation in polyurethanes, both for checking our own SRM's and for investigating the range of variation in commercial polyurethanes.

Characterization of Gas Research Institute Polyethylene

Polyethylene is widely used for piping in gas distribution systems. It has been recognized lately that better coordination of research and development activities facilitating comparison of techniques and test data would result if a single well characterized resin were available to all research workers in the gas distribution and associated industries. Such a resin should be available from a single supplier over a number of years. As a result the Gas Research Institute and OSRM are supporting work on the characterization of two "linear low density" polyethylenes used in gas piping, one with pigment, the other without. The unpigmented resin has been designated SRM 1496; the pigmented, SRM 1497. This new type of polyethylene has a considerably higher in molecular weight than any of the polyethylene SRM's now available. Such a standard would be useful to the rest of the scientific community because there is a growing need for higher molecular weight polyethylene standards.

The melt flow rate, a widely used measure of polymer processing properties, has been measured for SRM 1496 and 1497 by ASTM method D1238-82 under three standard test conditions. The value obtained under one of these, called the melt index condition, will be certified. The other two melt flow rates will be given as supplementary information. Work required for the certification of the limiting viscosity number of SRM 1496 in 1,2,4-trichlorobenzene at 130 °C has been carried out. Estimation of the distribution in molecular weight of both materials by gel permeation chromatography as supplemental information is underway. The measurement of a molecular weight of SRM 1496 for certification is also planned.

Poly(methyl methacrylate) Standard Reference Materials

Three poly(methyl methacrylate) polymers with molecular weights of approximately 8,000, 30,000, and 120,000, which are designated SRM 1487, 1488, and 1489 respectively have been bottled. They have been examined by NMR to check chemical identity and tacticity. The uniformity of the materials has been checked by capillary viscometry measurements.

Capillary viscometry measurements have been used to determine the limiting viscosity number (intrinsic viscosity) of all three SRM's. The number-average molecular weight of SRM's 1488 and 1489 was previously determined by membrane osmometry, and certificates have been issued for both these SRM's. Measurements of weight-average molecular weight of SRM 1487 by ultracentrifugation are underway.

Revalidation of Polyethylene Standard Reference Materials

For a variety of reasons, it was deemed desirable to have a measure of assurance that the materials presently available for sale as three of our polyethylene Standard Reference Materials (SRM's) have not changed significantly since their original certification. Accordingly, we have measured melt-flow rate and limiting viscosity number under the same conditions as those used for the original certification of SRM 1475 Linear Polyethylene (Whole Polymer) and SRM 1476 Branched Polyethylene (Whole Polymer). For both properties and both SRM's, the differences between the values measured now and those originally certified are too small to provide significant evidence for any change in these materials. A similar comparison, using only limiting viscosity number, has now been carried out for SRM 1482 Linear Polyethylene (Narrow Molecular Weight Distribution), with the conclusion that there is no significant change in the material.

Self-Calibrating Gel Permeation Chromatography

Gel permeation chromatography (GPC) is a widely accepted 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 calibrants for each polymer measured 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 so-called "universal calibration" hypothesis, while useful, is limited to comparisons of polymers of similar shape and, in any event, is inadequate for quantitative determinations. Some instruments, one of which is commercially available, attempt to 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 on the variation of scattering with angle, normally required to give assurance that meaningful results are being obtained, is not available.

A light-scattering detector for the GPC has been designed and built which measures, in real time, scattered intensity as a function of scattering angle. The apparatus is controlled by a dedicated minicomputer in a way that allows scattering to be measured as a function of both scattering angle and concentration. Continuous monitoring of the variation of scattering with angle while the chromatogram is being obtained allows immediate identification of difficulties 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. In addition to molecular weight, the mean-square radius (radius of gyration) can be obtained as a function of molecular weight, at least in the higher ranges of molecular weight, providing useful information for the characterization of branched polymers. The second virial coefficient, a measure of polymer-polymer interactions of both current and continuing interest to solution-properties theorists, can also be obtained as a function of molecular weight.

Molecular Characterization

F. W. Wang, C. M. Guttman, A. J. Bur, P. H. Verdier, R. E. Lowry,
J. H. Shibata, R. E. Dehl, and E. S. Wu[1]

[1]University of Maryland, Baltimore County

Work in this subtask concerns the development of improved methods for characterizing polymeric materials, and the development of fundamental concepts related to the solution properties of polymers. Fluorescence measurements of polymer diffusion and polymer-polymer interactions will provide data that are needed for heat-joining of polymers, for designing polymerization reactors, and for producing molecularly reinforced composites. The theoretical studies of translational diffusion constants and chain-molecule dynamics will yield fundamental concepts that will not only guide the experimental work on polymer-solution properties but also give insight on the processibility and the end-use properties of polymeric materials.

Fluorescence Monitoring of Polymer Processing Parameters

Fluorescence spectroscopy is a tool which has the potential for broad applicability to the measurement and control of polymer processing parameters such as non-Newtonian viscosity, molecular orientation, extrusion and injection velocities, and the degree of mixing of product ingredients. The technique involves the excitation of fluorescent chromophores and subsequent monitoring and analysis of the radiated fluorescence spectra. In order to do this, it is necessary to dope the processing ingredients with a low concentration of fluorescent chromophores which are added as separate entities or chemically bound to the polymer molecule. Ideally, fluorescence monitoring can be used for all polymer systems (homogeneous, semi-crystalline, blends, compounds, both filled and unfilled) in which a sufficient dispersion of active chromophores can be attained. The concentrations of chromophore are usually extremely low (10^{-4} to 10^{-6} molar), and therefore, do not affect the materials properties of the final product.

The chromophores are chosen in accordance with their sensitivity to a particular processing parameter. Information regarding the behavior and spectra of many chromophores can be obtained from existing data and literature, but the application of this information to the measurement and control of polymer processing parameters is a new concept and will require significant development of the measurement technique and the fluorescence/rheology database. Techniques relating fluorescence spectra to rheological data are not available, but such a procedure must be developed in order to establish correlations which are independent of specific polymer systems.

The ultimate application is to use fluorescence spectroscopy as an on-line non-destructive probe for real-time monitoring of processing parameters. Optical fibers can be employed to transmit and receive optical energy to and from monitoring sites in the processing equipment. Optical energy which is sent to the monitoring site excites nearby chromophores which respond by radiating characteristic spectra. From an analysis of the spectra, processing conditions at the probe site can be determined.

The nucleus of a polymer processing program has been under development in the Polymers Division during FY87. We have concentrated our efforts on equipment development and experiments to investigate mixing, zero-shear viscosity, and molecular orientation. Partial support for this program has come from the NBS Office of Non-Destructive Evaluation and the Office of Naval Research.

The equipment, which we will be using to compile the fluorescence/rheology database, is designed to measure fluorescence spectra and rheological parameters simultaneously. It consists of a capillary flow apparatus which has been incorporated into a commercial fluorometer and a Weissenberg rheometer which is being fitted with optical fibers for the transmission of optical signals to and from the rotating elements of the rheometer. Using these pieces of equipment, we intend to measure molecular orientation as a function of shear rate by observing fluorescence anisotropy of a chromophore chemically bound to a polymer chain. For the capillary experiment, the shear rate is varied by changing the hydrostatic pressure applied to the polymer solution flowing in the capillary. Construction of the capillary apparatus is complete, and the feasibility of the measurement technique has been demonstrated.

A chromophore, which we will employ in the capillary flow experiments, consists of a bifunctional anthracene molecule which will be bound to polybutadiene so that the fluorescently active anthracene is at the center of the polymer chain. The chemical procedure to do this has been established and the synthesis is underway.

A mixer, which incorporates co-rotating and counter-rotating shearing elements and glass walls for viewing fluorescence, has been constructed. The shearing elements of the mixer rotate at 10 rpm creating a moderate shear rate. This mixer was used to monitor the mixing of polybutadiene, molecular weight 3000, and aluminum oxide, grain size 14 μm. Prior to mixing polymer and filler, the polymer is doped (10^{-4} molar concentration) with coumarin 30, a fluorescent chromophore which is excited at 458 nm with an argon ion laser light source. The fluorescence intensity from the front surface of the mixer is observed as a function of mixing time. For short mixing times, wide variations in fluorescence intensity were observed as chromophore rich and poor regions of the specimen were brought into and out of the light beam by the mixer blades. For a mixture of 67% by weight of aluminum oxide in polybutadiene, we observed that, after 2 hours of mixing, the fluorescence intensity remained constant. This is our criteria for uniform mixing. Mixture uniformity of this specimen was qualitatively verified by using an optical microscope to view a 100 μm thick smear on a glass microscope slide. Pictures taken in transmission display a uniform dispersion of particulate in the polymer matrix.

In other experiments, we have made observations of the dependence of the intensity of the fluorescence spectra from a doped polymer as a function of temperature at zero shear. The specimen was from a sample of copolymer of BAMO and NMMO which has potential use as a binder in propellant mixtures. Here, BAMO is bis(azidomethyl)oxetane and NMMO is nitratomethylmethyloxetane. Emission spectra were observed at 25, 60, and 95 °C from the dopant p-dimethylaminobenzylidene-malononitrile which was excited at 440 nm. We attribute the observed decrease in intensity with increasing temperature to the decrease in microviscosity in the vicinity of the relaxing chromophore as temperature increases.

Evanescent Wave Induced Fluorescence Spectroscopy of Adsorbed Polymers

Selectively probing molecules near an interface is important in improving our understanding in areas such as adhesion, chromatography, and biological fouling. At a more fundamental level, theories on polymer adsorption benefit from experiments that can verify and extend the theories. Since light that undergoes total internal reflection at an interface penetrates a short distance beyond the interface into the lower index of refraction medium, molecules in the rarer medium and near the interface can interact with the penetrating light. This light is evanescent since it decays exponentially with distance from the interface. The characteristic penetration depth is on the order of the wavelength of light. If molecules near the surface are intrinsically fluorescent or extrinsically labeled with a fluorescent chromophore, the evanescent wave preferentially excites these molecules and induces fluorescence. We thus have a sensitive, and spatially selective probe of the interfacial region.

Our evanescent wave induced fluorescence spectrometer utilizes a thin film optical wave guide as our high index of refraction medium. Due to numerous internal reflections and the discreteness of the guided wave modes in an optical wave guide, the fluorescence signal is enhanced and the penetration depth is precisely determined. The penetration depth of the evanescent wave depends on the internal reflection angle, the indices of refraction of the two media defining the interface, and the wavelength of our laser light. In addition, we also utilize a half-wave plate to rotate the polarization of the exciting laser light. In general, the evanescent wave induced fluorescence depends on the polarization of the exciting light, the penetration depth of the evanescent wave, the absorption and emission properties of the chromophore, and the spatial and orientational distribution of the fluorescent molecules.

Current studies focus on measuring the orientational distribution of polymers in solution near the interface. Excitation of chromophores by polarized evanescent light is followed by measurement of the fluorescence intensity. The orientational distribution of fluorescent chromophores is obtained from an analysis of the dichroism of fluorescence. Preliminary measurements on N, N'-Bis(2,5-di-tert-butylphenyl)-3,4,9,10-perylene-dicarboximide dissolved in toluene, and on intrinsically fluorescent poly(p-phenylene benzbisthiazole) (PBT) fibers demonstrate the feasibility of measuring orientation. We plan to investigate the orientational distribution of PBT dissolved in methanesulfonic acid near the surface of our wave guide.

Translational Diffusion Measurements of a Conducting Polymer in the Melt

Specific interactions between inorganic salts and polyethylene oxide (PEO) contribute to the unusually high ionic conductivity observed in PEO complexed with inorganic salts. Analysis of the extent of the interaction as well as the degree to which the interaction contributes to the ionic conductivity is a formidable task. Our experimental approach is to measure changes in the properties of PEO that result from the presence of inorganic salts. In particular, a sensitive probe of an overall change in the dynamic properties of a polymer induced by specific interactions is the translational diffusion coefficient.

We use the technique of fluorescence recovery after photobleaching (FRAP) to measure the translational diffusion coefficient of fluorescently labeled PEO complexed with salt in the melt. Initial FRAP experiments on PEO in the absence of salt have been performed. The measured diffusion coefficient serves as a guide in our current experiments on PEO in the presence of varying amounts of salt. We plan to obtain the diffusion coefficient as a function of added salt, molecular weight of PEO, and temperature. The data will then be compared to conductivity data and analyzed based on a theoretical framework consistent with existing polymer and conduction theories.

Diffusion of Polymers in Semi-Dilute Solutions by Photobleaching Method

Verification of theories of self-diffusion and reptation in semi-dilute solutions has been hampered by the lack of a rapid method for determining the diffusion coefficient of polymers. We have applied a novel method, called Fluorescence Recovery After Photobleaching (FRAP), to rapidly measure the diffusion coefficient of a polystyrene polymer in semi-dilute solutions. The measurements cover nearly two decades of concentration and also extend to the low-concentration regime. These results agree with a recent theory which predicts that self-diffusion coefficient varies inversely with seven-fourths power of concentration in the semi-dilute regime, and varies inversely with the one-half power of concentration in the low-concentration regime. In collaboration with Prof. E. -S. Wu of the University of Maryland, Baltimore County, we are now using the FRAP method to measure the diffusion of polymers in both a theta and a good solvent, as a function of shape, concentration, and molecular weight.

Translational Diffusion Constant of Linear and Branched Chains

With the advent of experimental equipment in which both static and quasi-elastic light scattering may be done on the same sample, the ability to obtain both a radius of gyration and a hydrodynamic radius on the same system is possible. For branched chains, this ability offers the hope of obtaining structural information about branching heretofore unavailable. Since the character and details of the branching of a polymer molecule determine its processability as well as its ultimate physical properties and mechanical strength, such information on branching is invaluable.

One theory relating the radius of gyration to the hydrodynamic radius is the Kirkwood-Riseman theory of the translational diffusion constant in solution. However, there has been found to be a discrepancy between the experimental value of the translational diffusion coefficient of a polymer molecule in dilute solution and that obtained from Kirkwood Riseman theory using an analytical Gaussian model of the chain. The discrepancy is 15% for linear chains and nearly 50% for the ideal star branched chains studied.

Current work at this laboratory approaches this problem in various ways. In one, the hydrodynamic radius is computed using the Kirkwood-Riseman formulation for both linear and branched chains created by a computer simulation in which both excluded volume and interaction energies are included. These calculations have shown that about half of the 15% deviation found between theory and experiment can be explained by this modeling. Also, Monte Carlo chains have been created in which corrections only up to the second cluster integral or the second virial coefficient are included in the modeling. Such chains at the theta point are akin to the so called "true" self-avoiding walks. The importance of the third and higher cluster terms on properties like radius of gyration and hydrodynamic radius for both linear and branched Monte Carlo chains is being investigated.

In a second approach, analytical modeling was done on chains in which local chain structure but not excluded volume is taken into account. Earlier work showed that the analytical model currently available, which is used to compare theory and experiment, shows a very slow approach to its large molecular weight, M, limit. It is only in this limit that the Gaussian theory and experiment can be meaningfully compared. Thus corrections for large M values used to compare with experiments were not possible even for polymers of high molecular weight. Currently analytical work is being pursued in which both local structure and long range exclusion is taken into account in the same theory.

Characterization of Polyimide Polymers by Fluorescence Spectroscopy

Polyimide polymers are important in electronics and associated industries because they have properties suitable for photoresists and thermally stable insulators. In collaboration with scientists from AT&T, we have initiated a project to monitor the formation of polyimide polymer from p-diaminobenzene and 3,4,3',4'-biphenyl-tetracarboxylic dianhydride. The formation of the polyimide polymer from the poly(amide-acid) is accompanied by red shifts in the excitation and emission spectra. Therefore, the formation of the polyimide polymer can be monitored by measuring the increase in the fluorescence intensity at 560 nm when the sample is irradiated at 460 nm.

Fluorescence Spectroscopy of Rod-like Polymers

Recently, heterocyclic rod-like polymers, exhibiting thermal and oxidative resistance as well as superior mechanical properties, have attracted considerable interest. The high strength of these polymers arises from their ability to achieve a high degree of molecular order during film or fiber processing. Such order arises from the high degree of rigidity that these polymers show as well as the degree of interaction the polymers have with themselves and the surroundings. Even in solution, the polymers show anisotropic liquid crystalline states as well as isotropic states. In all states the polymers seem to exhibit a fully extended configuration.

In cooperation with the Materials Laboratory of the Air Force Wright Aeronautical Laboratories (AFWAL) we are developing fluorescence methods to study single chain and multiple chain properties of these systems. By looking at the time-resolved fluorescence intensities from dilute solutions of the polymers, we hope to provide an estimate of the torsional rigidities of these polymers which we expect will relate directly to their performance properties. From studies of the fluorescence of the solutions of these polymers as a function of concentration, we hope to characterize the polymer-polymer interactions as well as the degree of order in the various phases.

We have found that a dilute solution of poly(p-phenylene benzobisthiazole) (PBT) in methanesulfonic acid shows fluorescence anisotropy, indicating that the rotational relaxation time of PBT is much longer than 185 ps, the fluorescence lifetime of PBT. We have also measured the fluorescence anisotropy of a PBT fiber to characterize the orientation of PBT molecules in the fiber.

Fluorescence Studies of Polymer Solutions

Current interest in solution properties of polymers focuses on the shape of the polymeric chain in dilute solutions and the chain's interactions with itself, with other chains, and with solvent. The fluorescence quenching study provides information on many of these properties. The chemistry of attaching fluorescent and quenching groups to a polystyrene chain has been worked out and chains with varying concentrations of fluorophores and quenchers have been made. Preliminary experiments on the properties of single chains in solution have been done. Theoretical development establishing the relationship between the fluorescence properties of isolated chains or two chains in solution and other chain properties is being carried out in connection with the experimental studies. Our long range plan is to study the interchain properties of the polymer in more concentrated systems so we will be able to obtain properties of polymers in blends.

Dynamics of Polymer Chains

The dynamic behavior of polymer chains is important to improving both characterization and processibility of polymers. The principal methods used to estimate molecular weight, in particular gel permeation chromatography which is the only method available at present for estimating the distribution in molecular weight, are dynamical nonequilibrium experiments which depend in part upon the relaxation of polymer chains in dilute solution. In its present state, the theory of these systems does 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, could provide the basis for more efficient processing and better fabricated end products. A major shortcoming of the present theory is its inability to treat excluded volume and chain entanglement effects. 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 and serve to guide the development of better theoretical treatments.

We have completed a study of the effects of varying the lattice and the elementary move rules upon the dynamical behavior of bead-stick models both of polymer chains constrained to remain on three-dimensional lattices and of chains not so constrained. The chain-length dependence of the effects of self-entanglement and excluded volume upon long relaxation times depends upon the presence or absence of lattice constraints, but appears to be independent of the type of lattice used. The behavior of the translational diffusion constants roughly parallels that of the long relaxation times. A paper describing these results has been published.

MECHANICAL PERFORMANCE OF POLYMERS

The Mechanical Performance Group provides data, standards, and concepts of the mechanical properties of polymeric materials, their long term performance and the relationships among structure, mechanical properties and performance. The effort is divided equally between structure determinations and mechanical behavior. The Group has augmented its methods of structure characterization based on optical and electron microscopy, solid state NMR and vibrational spectroscopy with scanning tunneling electron microscopy. Techniques have been developed and are under development to prepare polymer samples for scanning tunneling electron microscopy. Applications of the technique to polymer science and technology include determination of molecular aspects, such as branch type and distribution, as well as the morphology of the precursors of fibrillar morphology in polymers. Branch content and distribution affect useful mechanical properties of polymers such as stress crack resistance and creep resistance. These data would augment results obtained with an NMR method which has been devised to measure the distribution of branches among the crystalline and non-crystalline phases of semicrystalline polymers. Information of the precursors of fibrillar morphology will aid in the design of methods to process polymer fibers to obtain high specific strength and stiffness.

The other half of the effort is concerned with elucidation of the mechanical behavior of polymeric materials and includes phenomenological descriptions of relationships between stress relaxation and creep data, single step vs. multiple step mechanical deformation or loading, the phenomenon of physical aging of polymer glasses, and experimental validation of the theory of reptation through careful experiments on cyclic polymer molecules that cannot reptate in the conventional sense. Mechanical characterization has been conducted on polystyrene gels to determine the nature of the structure of these materials in the gel state. NMR experiments have been conducted on the same gels to obtain a consistent picture of the structure of polymers in the gel state.

FY 87 Significant Accomplishments

- The branch composition was determined for polyethylene standard reference materials of the sort used in natural gas distribution piping and joints. These PE SRMs are linear low density polymers in which the side groups have been incorporated into the molecules to improve mechanical properties. This work will help the sponsoring Gas Research Institute to improve quality and performance of plastic gas pipe.

- A new constitutive equation was derived to overcome some of the deficiencies of the BKZ theory as applied to nonlinear behavior of incompressible, isotropic fluids. The new equation describes well the shear stress and normal stress response data to both single and double step stress histories for a 16.3% polyisobutylene solution in mineral oil.

- Scanning tunneling electron microscope images were obtained for small bundles of polymer molecules dispersed on a metal substrate. This result offers encouragement that the instrument may successfully image polymer molecular structure and detailed morphology of polymer structures.

- Current published models of the gel structure in isotactic polystyrene/decalin gels were corrected and refined with NMR data. High decalin mobility precludes the possibility of a polymer/solvent complex. Relatively high polymer mobility is indicative of small gel particle size and plasticization of the styrene by the decalin.

Characterization of Polymer Structure and Deformation Process

B. M. Fanconi, F. A. Khoury, G. B. McKenna, D. H. Reneker, D. L. VanderHart, E. Perez[1], B. F. Howell[2]

[1]Instituto de Plasticos y Caucho, Madrid, Spain
[2]David Taylor Naval Laboratory, Annapolis, MD

The Morphology of Crystallizable Polymers: The Development of Spherulitic Structures in Isotactic Polystyrene

The microscopic spherulitic structures which are commonly formed over a wide range of undercoolings when polymers are crystallized from the molten state usually evolve from lamellar (chain-folded) single-crystal-like precursors. The lateral growth habits of the precursor crystals reflect the crystallographic symmetry of the unit cell of the polymer, which is hexagonal in the case of isotactic polystyrene (i-PS) . The nature and origins of the 'degenerative' growth processes which govern the transitional stages of development of these precursors into the spherically symmetrical radiating array of long and narrow lamellae which constitute the mature stages of development of spherulites, remain to be fully elucidated with regard to the following three main features: (a) The three-dimensional details and the causes of the profuse interlamellar splaying. (b) The extent of the influence of impurity (i.e. low molecular weight or stereo-irregular chains) segregation on the progressive change in the lateral growth habit of the lamellae from hexagonal (in the case of i-PS) during the early stages of growth of the precursor crystals, to 'fibrillar' at the more advanced stages of spherulite growth. (c) The relationship, if any, between interlamellar splaying and the degeneration (hexagonal to fibrillar) of the lateral growth habit of the lamellae.

New insights into the three above mentioned features, in the case of the formation of i-PS spherulites, have been obtained following the discovery that amorphous i-PS dissolves readily in amyl acetate at room temperature whereas crystalline i-PS does not. This differential dissolution behavior has been used to excise spherulites at different stages of development from bulk partially crystallized polymer. The morphological characteristics of the excised incipient spherulites were then examined with a scanning electron microscope.

The following results have been obtained to date. (1) Interlamellar splaying is manifested prior to the occurrence of any distinct transition in the lateral growth of lamellae to the fibrillar habit. (2) It remains unclear whether interlamellar splaying is mainly a consequence of the segregation of impurities between lamellae. Available evidence indicates however that splaying is due, in part, to the lamellae having intrinsically curved conformations. This feature is probably due to buckling under the influence of the bulkiness of the chain folds. Additional evidence which supports this latter view, as distinct from any effects due to impurity segregation, stems from some exploratory experiments on the crystallization of i-PS from dilute solutions in which any effects due to impurity segregation are minimized. Yet, multilayered crystals in which the constituent lamellae exhibit splaying as well as curved conformations akin to those in the melt grown incipient spherulites were grown from the dilute solutions. (3) Interlamellar links were observed between the fold surfaces of overlapping lamellae. The occurrence of the links was more pronounced the lower the crystallization temperature and is clear evidence of irregularities in chain folding.

Continuing work in this project will include: (i) an investigation of the role of screw dislocations in the proliferation of lamellae in the course of the evolution of crystal precursors into spherulites; (ii) a more detailed study of the lateral growth habits and non-planar conformations of i-PS crystals grown from dilute solutions.

Small Defects in Polyethylene

A family of five crystallographic defects of three classes (two dislocations, 2 disperations, and one disclination) which constitute the known family of crystallographic defects that primarily involve only one polymer chain were described for polyethylene. Crystallographic defects satisfy the condition the atoms surrounding the defect are found closer to lattice sites as the distance from the center of the defect increases, and at large distances the crystal is essentially perfect. This condition insures that the extra energy required to create the defect is limited. Only a few kinds of defects satisfy the condition.

The extra energy associated with each defect in an otherwise perfect polyethylene crystal was computed. The crystal model used consisted of a central chain containing the defect with 18 zig-zag chains in two shells around the central chain. The zig-zag chains each had 60 carbon atoms. The conformation of each defect, placed near the center of the central chain, was adjusted to minimize the sum of the interatomic interactions. A closely related procedure was used to calculate the energy per chain at boundaries where each chain contains an identical partial dislocation or partial disclination.

The characterization of these well defined defects and partial defects greatly simplifies the establishment of connections between atomic and macroscopic scale phenomena in crystalline polyethylene. The defects described in this work are nanometer scale molecular mechanisms that diffuse along the molecules and translate them, rotate them, transfer free volume, accommodate structural singularities, bring reactive sites together, and more. In concert with a hierarchy of larger structures, such as entanglements, larger dislocation loops, and folds, these defects mediate the physical properties of polyethylene. Crystallographic defects are not restricted to polyethylene and can be generalized to all other crystalline polymers. Modeling of the interaction of the defects with each other and with morphological features such as folds or "impurity" structures such as branches offers a way to improved understanding of the larger scale mechanical and physical properties of crystalline polyethylene.

Morphology of Thin Polymer Films and Single Molecules

A primary goal of this work was to develop techniques for producing very thin polymer samples on conducting substrates of carbon, graphite, or metal. Layers only one molecule thick or discontinuous layers composed of a random network of very small fibers or even single chains were sought. Such samples are candidates for examination using scanning tunneling microscopy.

Several techniques based upon dispersing single polyethylene molecules in a dilute solution and collecting them on a conducting substrate were investigated. At the lowest concentrations, dense equiaxial particles with a volume equal to that of a single molecule were collected. At higher concentrations (or higher molecular weights), entanglements of the molecules in solution occurred. These entanglements persisted if the solvent was removed rapidly, so that networks having branches with diameters less than 100 Å were obtained. The concentration at which network forming entanglements were observed was about a factor of 10 smaller than the concentration at which spheres having a radius equal to the radius of gyration of the randomly coiled polymer molecule would touch. At higher concentrations, the propensity of polyethylene to form folded chain lamellar crystals was manifest.

The technique of broadest applicability was that of spreading a dilute solution of the polymer on the surface of a liquid that was immiscible with the solvent to produce a very thin film which was then stained with ruthenium tetroxide. This procedure was used to investigate polyethylene and other polymers. The polymers examined in this way include low density polyethylene, high and ultrahigh molecular weight polyethylene, isotactic and atactic polystyrene, poly-gamma-benzyl-L-glutamate, polyether ether ketone (PEEK), a block copolymer of deuterated polystyrene and polymethylmethacrylate, polybutadiene and a polydiacetylene called poly 4BCMU which has a rigid backbone with polar groups attached through short flexible linkages.

The films produced in this way were several molecules in thickness. Reproducible features of molecular scale that were characteristic of each polymer were observed using transmission electron microscopy. These features included regions that were equal to the molecular diameter and several nanometers in length, in an arrangement that suggested the top layer of a plate of spaghetti. In the block copolymer, since polymethyl methacrylate stains much less intensely than polystyrene, it was seen that although the molecules were randomly intermixed, light and dark regions with volumes equal to the volume of each block pervaded the sample, as if the blocks were separated in the sample. The polyethylene films were very disordered, but showed evidence of a tendency to crystallize. The poly 4BCMU sample showed long straight lines separated by a distance of 6 angstroms, which is commensurate with the width of the molecule with its polar groups in contact with the water, and also consistent with the stiffness of the backbone.

This work showed that direct examination of polymer molecular structures to produce information never before collected is possible with contemporary electron microscopes which have atomic scale resolving power. Although chemical changes produced by the electron beam remain a serious problem, staining with electron dense atoms such as ruthenium permit high resolution images of interesting molecular scale features to be made.

Observation of Fibers of Polytetrafluoroethylene with the Scanning Tunneling Microscope

Polytetrafluoroethylene (PTFE) is prepared commercially in the form of small particles called dispersion particles. Electron microscopy shows that if a dispersion particle is brought into contact with a solid surface, it adheres strongly at the point of contact. When the particle falls off or is brushed off, a long and very slender fiber of (PTFE) is drawn out of the particle and remains attached to the surface. The fiber diameters observed range from around 20 nm to less than 2 nm. The lower limit observed is set by the grain size of the shadowing material used so that fibers with even smaller diameters may be present on the surface. The length of the fibers is typically a micrometer or more.

A dense network of such fibers on an evaporated gold film was examined in the scanning tunneling microscope. Linear features with cross sections of 10 nm or less were found. No such linear features were found on gold films that did not have the PTFE fibers. The position of the linear features changed during repeated scans as if the fibers were moving slowly and somewhat independently. The fibers with the larger diameters moved much less.

These observations show that the scanning tunneling microscope is sensitive to the position of a polymer fiber on a conducting substrate. It remains to elucidate the interesting features of what must be a very complicated set of interactions between the scanning tip and the polymer fiber, and to explore the possibilities of observing atomic scale features of polymer molecules.

Characterization of Solid Polymers by NMR

In the description of the experimental work which follows, a major emphasis this year has been to develop the capability termed CRAMPS (combined rotation and multiple pulse spectroscopy) on protons. In this technique one can simultaneously quench proton spin diffusion (the magnetization transport process whereby domain sizes are deduced) and produce relatively high-resolution proton spectra in solids. A major area of application of the CRAMPS technique was to determine domain dimensions in polymer blends.

In work sponsored by the Materials Laboratory, Wright-Patterson AFB, OH, we have used CRAMPS to study domain sizes in a blend, consisting of 60% poly(phenylenebenzobisthiazole) (PBT) and 40% nylon 66, which was coagulated out of methane sulfonic acid, washed, and compression molded at 255°C. This sample had been studied previously using two other NMR schemes, all based on proton spin diffusion, in which either proton lineshapes or ^{13}C cross-polarized intensities were analyzed in order to establish proton polarization levels associated with the two polymer components. Both of these approaches suffered from recognized systematic errors which characterized the early period (about 1 ms) of spin diffusion. The CRAMPS version of the spin diffusion experiment was demonstrated to give results superior to the other approaches. Minimum domain dimensions averaging 5 nm were deduced from these results.

A second problem was undertaken in conjunction with Dr. Loon-Seng Tan at the University of Dayton Research Institute. Dr. Tan has been synthesizing polymers using intimate mixtures of two highly aromatic monomers, a bisbenzocyclobutene (BCB) and a bismaleimide (BMI). These substances polymerize thermally and yield a material with a single high T_g and promising mechanical properties. In concept, both monomers are bifunctional and could form a linear chain of alternating BCB and BMI units. In practice, each monomer can also thermally polymerize with itself; moreover, since each BCB monomer undergoes two ring-opening reactions, BCB can also become tri- or tetrafunctional in its polymerization, thereby providing a cross-linking route. We investigated whether ^{13}C cross-polarization, magic-angle-spinning (CPMAS) spectra could help elucidate the nature of the reaction in equimolar mixtures of BCB and BMI. While the above investigation is still underway, the following observations and conjectures have been made, based on the CPMAS spectra of samples of pure BCB or BMI (cured or uncured) as well as the cured copolymer:

- The cured copolymer spectra have certain identified resonances, not in agreement with an alternating BCB-BMI chain; notably, an unprotonated aliphatic carbon resonance appears which, based on its chemical shift position is associated with homopolymerization of BCB since it also appears in this product.

- A weak line in the methyl region is observed which probably arises from a protonation reaction when the cyclobutene ring opens.

- A preliminary and approximate estimate of the fraction of BCB-BMI bonds relative to the competing homopolymerization reactions is 0.5.

Investigation of the Intimacy of Mixing in Blends of Poly(etherimides) (PEI) and Poly(benzimidizoles) (PBI)

The cited polymer blends can be prepared so that they exhibit a single T_g which suggests intimate mixing on a molecular scale. To test this hypothesis, solid-state proton NMR experiments were conducted.

The first kind of experiment was based on the idea that, because of proton spin diffusion, an intimately mixed polymer system ought to exhibit only a single $T_{1\rho}^H$ relaxation time, whereas a phase-separated blend should exhibit a superposition of two relaxation times, which should be more typical of each homopolymer. This test was carried out at a temperature where the $T_{1\rho}^H$ of one of the components was both short and very different from the other. The conclusion was that mixing was intimate on a scale of at least 5 nm. This experiment does not differentiate signals arising from the individual components spectrally; all information is deduced from an analysis of the signal amplitudes with time in the relaxation experiment.

The second experiment involved the CRAMPS technique since the achievable proton resolution permitted a distinction between methyl protons and all aromatic protons. The PEI repeat unit consists of 6 methyl protons out of 24, while the PBI repeat unit possessed only aromatic protons. By monitoring the time required for all protons to equilibrate at the same polarization level following the establishment of a polarization gradient between the methyl and aromatic protons, it was concluded that the PEI and PBI were mixed on a scale of 3 nm. Therefore, the CRAMPS technique yielded information about the intimacy of mixing on a scale significantly smaller than could be sensed by the more conventional $T_{1\rho}^{H}$ test, even when the latter was optimized by choice of temperature.

Isotactic-Polystyrene/Decalin Gels

The motivation behind this study is to see whether NMR studies confirm two models which have appeared in the literature, namely, that a polymer/solvent complex forms and that the solid phase in the gel consists of a new polystyrene form different from the commonly found 3_1 helical form. Samples of isotactic polystyrene (i-PS), 25% by weight in either cis- or trans-decalin were examined. These samples are designated iPS-c-D and iPS-t-D. Conclusions are summarized as follows, based on variable temperature proton studies as well as room temperature ^{13}C cross-polarization spectra, including one CPMAS spectrum.

- The mobility of the decalin molecules in the gels is much too high for any stable polymer/solvent complex.

- The i-PS resonances consist of a broad and narrow component over most of the gel temperature range, prior to solvent freezing. Both the broad and the narrow components have monotonic changes with temperature, suggesting that the flexible chains, passing through the solvent at one temperature, will be slowly 'reeled in' by the solid phase as the temperature is lowered. Moreover, this is a reversible process.

- There are indications from the CPMAS spectra that the structure of the i-PS in the gel at room temperature is more ordered than the glass, although the linewidths are not as narrow as in a 3_1 helical crystal preparation. The greater ^{13}C linewidth, however, may be a result of forming smaller ordered domains in the gel. Proton results are suggestive of small domain sizes. Proton linewidths are about 10% narrower and relaxation times are shorter for the broad component of the gel compared to those for the glass or the 3_1 crystals at the corresponding temperature. Therefore, the solid phase of the i-PS/decalin gels shows a greater molecular mobility compared to both the glass and the 3_1 helical crystals and this, in turn is consistent with small domains and a high surface area. These latter observations are also consistent with the presence of a small amount of decalin acting as a plasticizer.

- The freezing behavior of the two solvents of the i-PS solution was also investigated since DSC data on the solvent freezing behavior strongly suggested a polymer/solvent complex. It was verified that substantial portions of the solvent remained mobile when solvent freezing first begins. Again, in agreement with DSC, the cis-decalin freezes more slowly than the trans-decalin. Our current hypothesis to explain this freezing behavior is that the i-PS chains or small clusters of chains which pass through the solvent greatly restrict the growth in size of the solvent crystals, and that cis-decalin is most affected since its heat of fusion is less than that of the trans-decalin.

Mechanical Properties Measurement and Modeling

J. M. Crissman, G. B. McKenna, L. J. Zapas, A. Brenna[1], D. J. Plazek[2],
K. L. Ngai[3], R. W. Rendell[3], and J. M. Guenet[4]

[1]Center for Industrial Research, Oslo, Norway
[2]University of Pittsburgh, Pittsburgh, PA
[3]Naval Research Laboratory, Washington, DC
[4]Institut Charles Sadron, Strasbourg, France

Reference Standard Polyethylene Resins and Piping Materials

Polyethylene has rapidly become the material of choice for gas distribution piping in the United States and currently accounts for the 80% of new installation and essentially all new piping which is non-metallic. The Gas Research Institute (GRI) is sponsoring a program at NBS to provide reference materials for use in research pertaining to natural gas distribution systems. This program includes the procurement and characterization of both pigmented and unpigmented pipe resins, as well as piping and joints prepared from the pigmented resin.

During work the previous year, an important observation was made concerning differences in the melt flow rate for the two types of joints. Whereas the melt flow rate for the "butt fusion" tee joint was in the range from 1.103, to 0.988 g/10 min, that for the "socket" tee joint was in the range from 0.605 to 0.411 g/10 min. The melt flow rate for the starting resin was in the range from 0.878 to 0.758 g/10 min. A similar result was found for two types of pipe, where in both cases the melt flow rate was measurably lower for the pipe material than for the starting resin. It was concluded that the changes which had occurred were a consequence of the processing. The work done during the current year has been concerned principally with examining more closely the observed differences in melt flow rate and to establish whether or not this phenomenon is general to the entire lot of piping and joints.

Since the melt flow rate of the resin can change as a result of the processing, it is important to determine whether mechanical performance is affected as well. The occurrence of chain scissions, especially within the high molecular weight components of the molecular weight distribution, can have a detrimental effect on the long term mechanical behavior. On the other hand, crosslinking may have a beneficial effect. One measure of performance which is sensitive to degradation or crosslinking is the environmental stress-crack resistance (e.s.c.r.). Degradation results in decreased lifetime under standard e.s.c.r. test conditions, whereas crosslinking may have the opposite effect. A second measure of mechanical performance which is sensitive to molecular weight and molecular weight distribution is creep. Parameters such as the maximum stretch attainable and the tensile strength will both be sensitive to degradation or crosslinking.

The e.s.c.r. of material taken from the two types of tee joints is currently under investigation. To date, four specimens of material from the socket tee joint have been tested. Two of the specimens failed after approximately 5000 hours and the other two specimens remain under test. Two specimens of material from the butt fusion joint are currently under test, and as of this date neither has failed after approximately 1000 hours.

Specimens for the creep experiments were cut from the same sheets of remolded joint material from which the specimens for the e.s.c.r. tests were cut. Four sets of creep data were obtained at applied stress levels of 10, 12.5, 15, and 20 MPa on specimens taken from both types of joints. Two features of the resulting data have relevance to the observation that the melt flow rate of the two materials differs by more than a factor of two. First, in the region of very large strains, where the thinned down, or necked, portion of the specimen has propagated completely through the straight section of the specimen, the creep curves reach a plateau and become essentially flat thereafter. In this region the stretch ratio varies from about 6 to 9 depending upon the level of applied stress. At the three highest levels of applied stress, the strain is consistently greater in the specimens from the butt fusion joint than in those from the socket joint. This trend is consistent with the behavior of other polyethylenes where it is found that the higher the molecular weight the less the maximum stretch is achieved prior to fracture.

The most striking difference in behavior occurs for the two specimens under the smallest applied stress of 10 MPa. At times up to about 10^3 minutes and a strain of about 10%, the creep curves essentially superpose. However, beyond this time the behavior differs significantly. The creep curve for the material from the butt fusion joint is almost identical to that for material molded directly from the starting resin. On the other hand, the material from the socket joint shows significantly less creep at the longer times. For example, at the time at which the specimen of material from the butt fusion joint had necked, the material from the socket joint had attained only about one one-half the value of strain.

Taken together, the two different sets of results from the creep experiments suggest that the differences in material which resulted from the processing are sufficient to alter the mechanical behavior. The creep data are consistent with the melt flow rate measurements to the extent that they both suggest that the material in the socket tee joint has a somewhat higher molecular weight than that from the butt fusion joint. The differences in behavior at the very long times under the smallest applied stress may well have implications with regard to the phenomenon of slow crack growth. Further work is underway to better define the differences in creep behavior at the very long times.

The Effect of Molecular Architecture on the Viscoelastic Properties of Melts

Work has continued to characterize the behavior of narrow fractions of cyclic polystyrene molecules synthesized at the Institute Charles Sadron in Strasbourg, France and those synthesized by B. A. Hostetter and L. J. Fetters at the University of Akron. During the past year new viscosity data were obtained on two melt fractions and a stronger comparison made with results obtained by J. Roovers at the National Research Council in Ontario, Canada on his own fractions. The current work does not change the major conclusions of prior work, i.e., that cyclic macromolecules, although they cannot reptate, move as easily in the melt as do linear chains. However, there are two slight changes in the conclusions made previously. First, the critical molecular weight for entanglement coupling, M_c, of the cyclic polystyrene is now estimated to be approximately 60000 (vs 40000) which is in agreement with the results from measurements of the plateau compliance. Second, the molecular weight dependence of the viscosity of the cyclic polystyrenes above M_c is now better represented by $\eta_0 \propto M^{3.7}$, which is a somewhat stronger power law dependence than that exhibited by the linear chains, i.e., $\eta_0 \propto M^{3.4}$.

The comparison of results with those of Roovers is based upon the value of the steady state recoverable compliance, J_e^o vs molecular weight, M_w. The Roovers samples exhibit a continuing and dramatic increase in J_e^o as M_w increases while our samples show a plateau at $M_w > 10^5$. This result is consistent with the presence of a high molecular weight content in the Roover samples. Furthermore, his samples have values of J_e^o which appear too low at low molecular weights. Such a result may indicate the presence of a high proportion of knotted rings.

Continuing efforts are being made to understand the reasons for discrepancies between the Strasbourg and Akron samples and those from Roovers in Ontario. The work raises fundamental questions about molecular architecture and chain dynamics.

Some Approximate Relations for the Analysis of Single Step Stress-Relaxation Experiments in Uniaxial Extension

In the determination of the single step stress-relaxation behavior there is the problem of a finite time being required, during the application of the step, to reach the desired strain, which introduces an uncertainty into the observed behavior at the early times. Some years ago, Zapas and Phillips derived an approximation which can be applied to shear stress-relaxation experiments in the region of linear behavior. Work is currently underway to extend their idea to measurements in simple extension. For certain systems, such as semicrystalline polymers, where some simplifying assumptions can be made, we have extended these approximations into the region of nonlinear behavior. The derivations are based on the assumption that, for the strain histories considered, we can use the Bernstein, Kearsley, and Zapas (BKZ) theory as a one dimensional description. To show the validity of the approximate relations, we have obtained data on a linear low density polyethylene copolymer at 26°C. The theory shows that for this particular system one needs only one experiment in order to obtain a good approximation to the nonlinear surface describing the single step stress-relaxation behavior. However, in practice a larger set of experiments may be necessary if the experiments involve very large deformations.

Nonlinear Viscoelastic Behavior of Polymeric Fluids

In an attempt to overcome some of the inadequacies of the BKZ theory as a description of the nonlinear behavior of incompressible, isotropic fluids, we have derived a new constitutive equation. For the case of simple shear histories, the shear stress is given by:

$$\sigma_{12}(t) = -\int_{-\infty}^{t} H_{*}[\gamma(t)-\gamma(\tau), t-\tau]d\tau + \int_{-\infty}^{t} F_{*}[\gamma(t)-\gamma(\tau), t-\tau] \int_{\tau}^{t} \phi[\gamma(\xi),\xi]d\xi dt$$

and the first normal stress difference, $\sigma_{11}(t)-\sigma_{22}(t)$, is given as

$$\sigma_{11}(t)-\sigma_{22}(t) = \int_{-\infty}^{t} H_{*}[\gamma(t)-\gamma(\tau), t-\tau][\gamma(t)-\gamma(\tau)]d\tau + \int_{-\infty}^{t} F_{*}[\gamma(t)-\gamma(\tau), t-\tau][\gamma(t)-\gamma(\tau)] \int_{\tau}^{t} \phi_{11}[\gamma(\xi),\xi]d\xi dt$$

where $\gamma(t)$ and $\gamma(\tau)$ are the shear strains at times t and τ.

For single step stress relaxation histories, one finds that the so-called universal relationship, i.e., $\sigma_{11}(t)-\sigma_{22}(t)=\partial\sigma_{12}(t)$ is not valid for this constitutive equation. Rather one finds:

$$\sigma_{11}(t)-\sigma_{22}(t)=\gamma[H(t)-F(t)\phi(\gamma)] + \gamma[F(t)\{\phi(\gamma)-\phi_{11}(\gamma,t)\}]$$

where the first term on the right hand side represents the strain times the shear stress and the second term is a "correction" term resulting from the nonlinear constitutive law.

Single step and two step stress relaxation histories have been obtained for a 16.3% polyisobutylene solution in Primol (proprietary mineral oil sold by Exxon) using a cone and plate geometry. The new constitutive law describes the shear stress and normal stress responses quite well. Of great importance is the finding that the ratio of the first normal stress difference divided by the product of the strain and the shear stress differs from unity, i.e., the so-called universal relationship is not valid. Specifically, we found that a double logarithmic plot of $[\sigma_{11}(t)-\sigma_{22}(t)]/\gamma\sigma_{12}(t)$ vs t yielded a straight line with slope 0.24. Though one could argue that the values of the above ratio at short times, which are smaller than unity, result from the machine compliance, we could find no reason for values higher than unity obtained at longer times, e.g., at 100 seconds the ratio reached a value of 1.5. Work is continuing to further substantiate this result. Tests of the new constitutive equations ability to predict material response to constant rate and load-unload types of deformation histories are also being performed.

Concentration Dependence of the Zero Shear Viscosity and Terminal Relaxation Time in Polymer Solutions

There is much current interest in polymer chain dynamics in entangled systems. Much of this interest has focussed recently on reptation and the Doi-Edwards tube model. In this work, we have used the Ngai model which describes relaxation in complex systems using a time dependent rate which results in two equations describing a single relaxation process. The first predicts a non-exponential relaxation function and the second an experimentally observed relaxation time which is shifted to longer times from the primitive relaxation time of the relaxing species in question. By assuming that a Rouse chain having a subunit which corresponds to the distance between molecular entanglements is the primitive relaxing species and that the friction factor in the Rouse model is indeed the "bead" friction (rather than the later postulated monomeric friction factor) we have been able to derive equations for the concentration dependence of the zero shear viscosity and terminal relaxation times in polymer solutions. The model also incorporates the molecular weight dependence. We find:

$$\eta_0 \propto \phi^x M^y \qquad (1)$$

$$\tau \propto \phi^z M^y \qquad (2)$$

where η_0 is the zero shear viscosity, ϕ the concentration, M the molecular weight and τ the terminal relaxation time. The exponents are found to agree well with experimental observations i.e., $x \approx 3.6$, $y \approx 3.4$, $z \approx 1.5$. An interesting result of the model is that the scaling exponents depend upon the shape of the relaxation spectrum.

The results of this work are also compared with reptation and scaling theories. The new results are found to agree better with experiment than the reptation or scaling results. In addition, it is pointed out that the reptation treatment does not agree with experimental observations for the concentration dependence of the self diffusion coefficient, while the scale theory appears to overestimate the concentration dependence of the zero shear viscosity. At this time the Ngai coupling model has not been extended to treat the concentration dependence of the self diffusion coefficient.

Isotactic Polystyrene Gels

Isotactic polystyrene (i-PS) gels can be formed by quenching solutions of i-PS in poor solvents to below their theta temperatures. The gels exhibit thermo-reversibility in the sense that they melt rather than decomposing. The structure of these gels and their mechanics of formation are somewhat controversial, although evidence exists that they form by a spinodal mechanism and the resulting large scale network structure is speculated to be the result of the growth of this originally spinodal network. The mechanical properties of these gels are complicated, and may reflect the underlying network morphology.

We undertook to investigate the phase behavior of i-PS/cis-decalin and i-PS/trans-decalin using Differential Scanning Calorimetry (DSC). We also studied the mechanical properties of the gels for different formation temperatures, aging times and molecular fractions having different molecular weights and polydispersities. Because the DSC was insensitive to such changes we have been unable to correlate the phase behavior with the observed mechanical properties, which are more sensitive to subtleties in structure than are the thermal properties of these gels.

The phase diagrams of the i-PS/cis-decalin and i-PS/trans-decalin gels were determined both upon formation and melting. The melting diagrams of the i-PS/cis-decalin gel indicate the existence of a monotectic and that of the i-PS/trans-decalin a singular point. In both instances, the results are consistent with the existence of a "solvated" phase at 26% i-PS/cis-decalin and 47% i-PS in trans-decalin. This interpretation, however, must be questioned due to NMR measurements carried out last year in this laboratory. An alternative explanation has yet to be found.

The mechanical property used to characterize the gels of i-PS in cis-decalin, trans-decalin and 1-chlorodecane, is the isochronal compression modulus. We have found that not only is the modulus concentration behavior unusual in that it shows non-power law dependence and "features" but its shape is independent of aging temperature and time, i.e., the E vs C curves can be superimposed simply by a vertical shift $b(T, t_a)$ where T is temperature of gel formation and t_a is the aging time at T. Thus, the modulus is

$$E(T,t_a,C) = E\ (T_o,\ t_{ao})/b(T,t_a) \bullet f(c)$$

where T_o and t_{ao} are reference temperature and aging time, f is a function of concentration alone, and b is the vertical shift factor.

We have found that both E and f are functions of the fraction molecular weight. The vertical shift factor (or modulus) only varies at $T \geq 0°C$, i.e., the gels do not age (or ripen) when formed at -10°C or -20°C.

Polymer Glasses - Thermodynamics and Kinetics

An article on polymer glasses was prepared as a chapter in the book Comprehensive Polymer Science, edited by Geoffrey Allen. The chapter reviews the thermodynamics of phase transitions as they apply to glasses and takes a critical view of attempts to establish the nature of the glass transition event using conventional thermodynamic measurements, e.g., PVT and Cp, to test the validity of the Davis-Jones relationships for second order transitions. Rather, it is argued that models of the glass transition should be tested for validity based upon their ability to predict changes in behavior due to changes in molecular or compositional variables. Extensive discussion is given to both the configurational entropy model and the free volume model and their ability to describe and predict changes in T_g with e.g., molecular weight, polymer blend composition, deformation, etc.

The chapter also presents an extensive discussion of recent developments in our understanding of the kinetics of glass formation and structural recovery. The phenomenology is explained and the equations which have been developed by several groups are outlined and discussed in terms of their ability to describe the phenomena that are observed experimentally. A section is devoted to the so-called τ-effective paradox and attempts to explain it. The discussion of the phenomenological models of glassy kinetics is complemented by a discussion of the Robertson-Simha-Curro free volume model of glassy kinetics. Finally, brief discussions are given of the results of recent computer simulations and the phenomenon of physical aging.

Durability Testing of Rubber Compounds for Tank Track Pads

K. M. Flynn and G. B. McKenna

Work has been carried out for the U.S. Army Tank-Automotive Command to evaluate the mechanical durability of three rubber compounds which the Army is considering for use on tracked vehicles. The original thrust of the program was to examine the creep rupture and fatigue failure behavior of the rubber compounds within the context of a cycle shifted failure envelope (CSFE) model of rubber failure which had been previously developed in this laboratory and successfully used to describe frequency and wave form dependencies of fatigue lifetimes of a carbon black filled butyl rubber. The obvious corollary to this objective was a further test of the validity of the CSFE failure model.

Work carried out to determine the failure envelopes under conditions of constant rate of loading, creep to rupture and zero-tension sinusoidal fatigue resulted in the surprising finding that the creep failure envelope and constant rate of loading envelope did not coincide, contrary to prior findings both in this laboratory and elsewhere. Furthermore, it was found that the creep failure envelopes determined at different temperatures were different. These results, i.e., the existence of a non-unique failure envelope make the simple form of the CSFE unusable for the rubber compounds in question. They further open to questioning the assertion usually found in the literature that the failure envelope is a unique description of failure in filled elastomers, even under simple loading histories.

The CSFE context, however, provided the framework to evaluate the relative durabilities of the three rubber compounds and to give to the Army the relative merits of the three compounds under tensile loading conditions at temperatures ranging from 23°C to 175°C.

PROCESSING AND RELIABILITY OF 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 predict performance, particularly long term durability.

To achieve these goals, the underlying science base, which is currently weak, must be significantly strengthened. The Composites Task is responding to this need by conducting long range, basic research to provide industry and other Government agencies with test methods, material properties data, and predictive models in the area of composite processing and performance.

The overall objective in this Task is to establish the scientific basis for the relationships between the generic parameters associated with formulation and processing and the properties important in the performance of the final material. The programs in this Task are divided into three highly interrelated areas: processing, structure, and performance.

Projects in the first subtask are further divided into two groups: the first group focuses on the development of new process monitoring techniques and the application of these techniques to the study of model systems; the second group is a smaller effort which involves the formulation of new material systems designed for radiation curing. Studies in the first area provide both new measurement methods for process monitoring and the improved scientific understanding that is essential for process control. The latter area centers around an other agency sponsored program to develop new vehicles for printing inks. The technology involved is also relevant to other systems where rapid and controlled cure are essential. Examples are; composite repair, adhesive bonding, and composite resins suitable for rapid fabrication.

The second subtask seeks to bridge the gap between processing and performance by developing techniques to characterize the structure of composite systems. Both macro-structure (i.e. flaws, defects, phase separated domains, etc.) and micro-structure (morphology, crystallinity, and the molecular network in crosslinked systems) are of interest. During the past year the work focused on the use of neutron scattering to study the development of the network structure during the cure of model epoxy systems.

The third subtask focuses on the determination of performance properties of composites and composite resins in three areas; the physical aging behavior of crosslinked glassy polymers, interlaminar fracture in composites and failure behavior in adhesive joints.

To conduct this effort, the Composite Task utilized cooperative programs and guest experts. An Institute wide Colloquium Series on Composite Materials brought many world renowned scientists to NBS for discussions. Cooperative efforts include programs with NASA Langley Research Center, the Department of Treasury, and the industrial research laboratories of Hercules, Hexcel, and Texaco. A joint program with Dr. A. J. Kinloch at Imperial College (London) continues. Projects with Mead Company, Dexter-Hysol, and Dr. John Gilmer of the University of Pennsylvania were initiated. Dr. Andre Lee from the University of Illinois joined the Group as a postdoc and Ms. Weijie Su from the Shanghai Institute of Pharma and Tech. in China completed her sabbatical as a visiting scientist.

FY87 Significant Accomplishments

- A new class of polymeric resins has been designed and synthesized as candidates for electron beam curable inks. These materials show very good drying behavior, viscosity, and water washability prior to cure. The latter property is essential for success in water-wipe intaglio printing. On-line printing experiments are currently underway at the irradiation facility at BEP.

- A percolation model was successfully applied to a theory of network formation in thermosetting composite resins where crosslinking reactions are not dominated by linear polymerization reactions. Neutron scattering and computer modeling results confirmed applicability of the theory.

- A model was developed for large strain deformations in thermosetting polymers. Small angle neutron scattering experiments showed little change in the average distances between crosslinks as a sample was deformed. This result indicates that the strain is accommodated via inter-chain rather than intra-chain deformation, and suggests a network unfolding mechanism.

- Growth of the crack tip deformation zone in structural adhesives was measured as a function of load up to the failure point. The results were found to be in good agreement with predictions of non-linear elastic-plastic finite element analysis, and gave confidence in improved understanding of failure in this widely used class of materials.

Processing Studies on Resins and Composites

S. S. Chang, B. J. Bauer, G. W. Bullman, B. Dickens, D. L. Hunston,
J. Phillips, W. J. Pummer, W. L. Wu, A. J. Bur, B. M. Fanconi,
F. I. Mopsik and F. W. Wang

On-line process control offers a promising approach to improving the speed and reliability of composite fabrication. To implement on-line process control, appropriate techniques for on-line monitoring and the corresponding knowledge and models relating the monitoring results to material behavior must be developed. The processing subtask adresses both of these needs. In addition, this portion of the composites program also includes a project with the Bureau of Engraving and Printing to develop resin systems that can be cured by electron beam radiation. The technology for radiation curing developed for inks is of great interest to the field of composites processing.

Process Monitoring for Composite Resins

Historically, process monitoring studies have focused on the cure of thermosetting resins. In recent years thermoplastics have become increasingly important. These two classes of materials can have different processing problems and consequently, different process monitoring techniques can be required. Both types of resin are being addressed in the NBS program, and some of the results from the past year are summarized below.

THERMOPLASTICS: Thermoplastic composites have potential advantages for recycling, repair, ease of fabrication, and raw material storage. Potential disadvantages include less solvent resistance and increased viscosity. Polymers with some crystallinity have improved solvent resistance, but their use requires that the crystallinity must be monitored and controlled during processing. Increased viscosity of thermoplastics results from their high molecular weight relative to uncured thermoset resins. This increased viscosity inhibits proper flow behavior. Higher processing temperatures improve flow, but also increase the danger of thermal degradation of the resin. At temperatures low enough to avoid degradation the resin may not flow well enough to eliminate all voids in the processed composite (consolidation). When highly loaded, as in short fiber injection molding, the viscosity of thermoplastics also provides a major barrier to achieving sufficient flow. Consequently, the monitoring of consolidation and flow during processing is needed.

This program develops techniques that can be used on-line to monitor the crystallinity and flow/consolidation behavior of thermoplastic composites during processing. Dielectric spectroscopy and ultrasonics were chosen to investigate crystallinity while fiber optic sensors and fluorescence spectroscopy are being evaluated as methods to measure flow and consolidation. Neat resin samples were used as a first step to evaluate the potential of these techniques.

<u>Crystallinity Measurement</u>: A recently developed high performance, high temperature polymer, poly(aryl-ether-ether ketone) known commonly as PEEK, was chosen as a model resin. A press is being modified so that molten samples of PEEK can be rapidly quenched to produce amorphous materials. These samples can then be converted to different degrees of crystallinity by annealing. Concurrently, a laboratory method, differential scanning calorimetry (DSC), is being developed to select appropriate annealing cycles for sample preparation, and to determine the final degree of crystallinity in the test specimens. These samples will be used to evaluate the sensitivity of potential on-line measurement methods for detection of crystallinity differences.

Initial DSC measurements used thin film samples of amorphous PEEK obtained from NASA Langley Research Center. When cooled normally from above the melting point, crystallinity of around 30% was obtained from these films. The crystallinity could be increased to 40% with special annealing procedures. Thus average degrees of crystallinity between 0% and 40% can be achieved with these films.

The crystallization behavior of PEEK has some resemblance to that of branched polyethylene; i.e., there is a wide spectrum of crystalline morphological perfection causing a wide spread of melting to occur between 200 and 340°C. Annealing at any particular temperature will cause an increase in the population of the crystals that melt at about 10°C above the annealing temperature at the expense of the populations that melt near or below the annealing temperature. A continuous rapid cooling temperature ramp generally produce a smooth melting curve. A slow cooling ramp however will yield a second major peak at about 325°C. Ten or more of these reorganization peaks can be resolved when special step cooling procedures are used (see figure 1). This result demonstrates that on-line monitoring techniques, which will measure only an average degree of crystallinity, may not always provide an adequate characterization of the sample.

Evaluation of Crystallinity by Dielectric and Ultrasonic Techniques: Clear differences were found in the dielectric properties of thin film samples of PEEK with 0% and 30% crystallinity. The results were complicated, however, by the presence of a conductive-like effect, due perhaps to additives or contaminants inside the film. The NASA samples were too thin (70 μm) for ultrasonic studies. For both measurements, more carefully prepared samples are required.

Flow and Consolidation: Three fiber optic methods have been investigated as potential techniques to monitor consolidation. For each method, an optic fiber sensor is placed between the plies of a laminate and the fraction of the total sensing fiber surface in contact with the resin is taken to be a measure of consolidation. One method is based on fluorescent probes such as those used in our previous studies to measure resin viscosity, and the other two use the refractive index difference between the resin and air (or other volatiles) to measure the fractional surface coverage. It was concluded that the technique involving fluorescent probes in combination with optic fiber sensors has advantages in terms of simplicity and sensitivity over a wide range of surface coverage.

For low temperature processing involving flow, fluorescence spectroscopy is being evaluated as an on-line measure of non-Newtonian shear viscosity. Fluorescence anisotropy can provide a measure of molecular orientation, and this can be used to develop a correlation between the increase in anisotropy and the decrease in non-Newtonian viscosity. A fluorescent chromophore will be chemically bound to the polymer molecule in order that the shear stresses are translated into orientation of the chromophore. Initial efforts are to design and develop the measuring equipment, and to identify and synthesize the fluorescent chromophore. Preliminary experiments on polybutadiene indicated that anisotropy can be observed to change with changes in applied pressure. Measurements will be made to correlate anisotropy with viscosity for a polymer solution and melt.

THERMOSETS: Thermosets generally have adequate flow during processing, but it is still important to monitor and control this flow if efficient fabrication is to be achieved. Thermoset processing is complicated by chemical reactions, and the major need is to determine the extent of reaction (degree of cure) at any

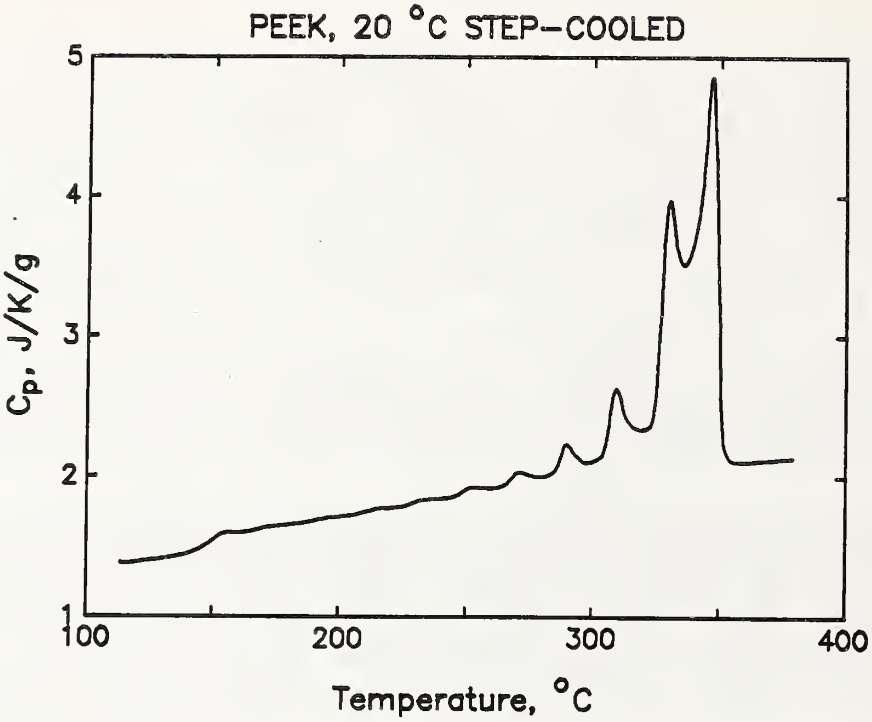


Figure 1: Heating curve for PEEK after slow cooling an amorphous sample in 20°C steps. Multiple melting peaks and the T_g are seen.

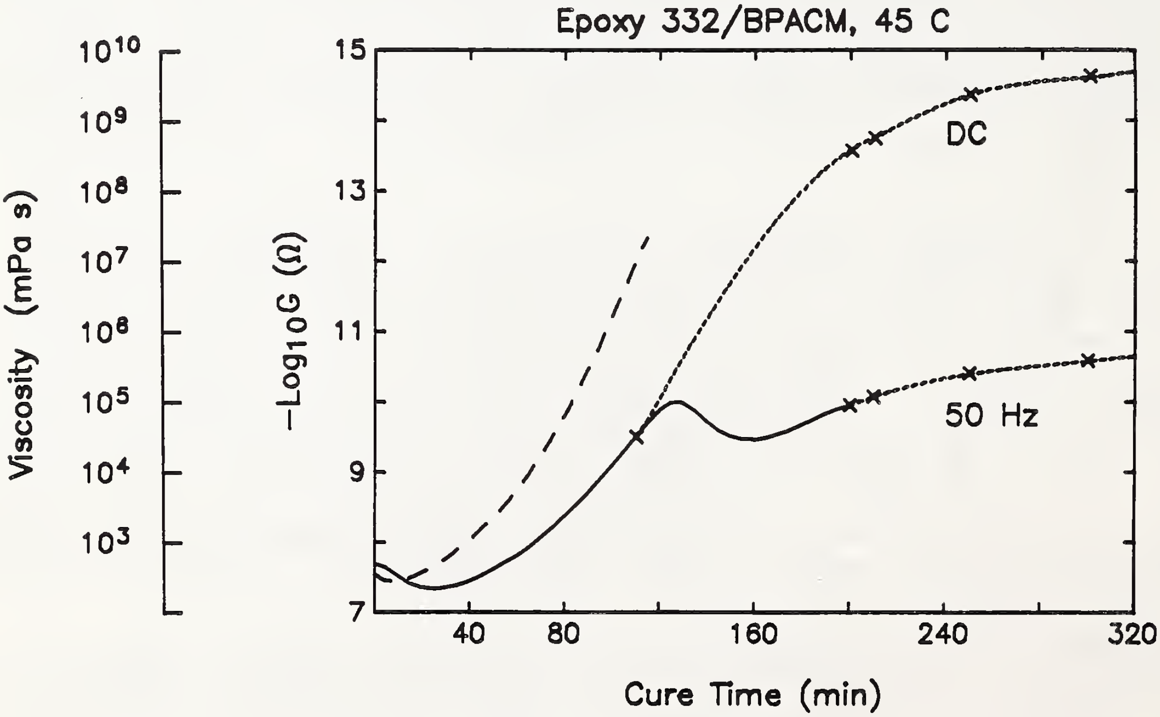


Figure 2: Cure monitoring of DGEBA-BPACM system at 45°C at 50 Hz and DC by viscosity (long dash) and dielectric measurements (solid and short dash).

given time and its relationship to other properties such as flow. A program to develop, maintain, and correlate a wide variety of cure monitoring techniques has been underway at NBS for several years. This program currently has available ten different process monitoring methods; some with on-line capabilities. These techniques can be grouped in terms of the properties they measure: 1) mechanical and transport properties (viscosity, dynamic mechanical measurements, ultrasonic shear wave attenuation), 2) thermal properties (differential scanning calorimetry), 3) electrical properties (conductance and dielectric loss measurements), 4) optical properties (various types of spectroscopies, and fluorescence techniques), and 5) chemical and structural properties (neutron scattering and size exclusion chromatography). Many of these techniques were described in detail in the past annual reports.

During the last year, improvements were made in several techniques. Dielectrics: The temperature controller for the dielectric spectrometer was improved so that the time required for the sample to reach equilibrium was significantly reduced. The modification increased the temperature response of the system by almost an order of magnitude. Ultrasonics: A high temperature furnace was constructed so that materials with cure temperatures of 150 °C or more could be measured.

Several thermoset systems were examined this past year. For example, the curing of diglycidyl ether of bisphenol-A (DGEBA) and bis-(p-aminocyclohexyl) methane (BPACM) was analyzed by many techniques including dielectrics. The dielectric data were used to extract the DC conductance at long cure times where the AC conductance (50 Hz) shows a glass transition peak. These data allow comparison of the steady shear viscosity with the reciprocal of the DC conductance (see figure 2). The correlation between these quantities departed from the direct proportionality predicted by one simple model.

Design and Synthesis of Radiation Curable Resins

Radiation curable resins combine rapid processability with exceptional process control. The design of such resins involves several trade-offs since radiation curable groups must be added to the resin without sacrificing desireable properties of the end product. This year work centered on improved electron beam-curable printing inks for the Bureau of Engraving and Printing. The general approach used should be transferable to other types of resins and other types of radiation such as UV or thermal radiation.

Spread sheet computer programs were used to estimate relevant properties of candidate resins based on their reactive groups, functionality, molecular weight, chemical type, etc. The programs also calculate the formulation to be used in the synthesis of the resin. This makes it possible to examine a wide range of possible structures and to identify promising candidates. The program was applied to water dispersible printing inks that can be cured by electron beam radiation. The water dispersibility is determined by the polyethylene oxide (PEO) content, and the cure rate is determined from the concentration and reactivity of the polymerizable groups. Viscosity is also an important consideration and is determined by the molecular weight and chemical nature of the molecular units. The results are summarized below.

Four types of resin have been synthesized. All contain polyethylene oxide (PEO) units, capped at one end with acrylate or methacrylate groups. The first type is based on a phosphazene (P3N3) center unit and is hexafunctional. The second type is a comb structure resin, with a polymeric backbone, pendant PEO arms, and acrylate ends. The third type is based on urethane bonds between PEO units capped with acrylate or methacrylate groups. The urethane resins are divided into two sub-types: those prepared with little or no participation of water in the reaction, and those in which water was an important ingredient. The fourth type is based on a tetrafunctional siloxane center extended with pendant PEO arms and methacrylate ends.

Resins containing phosphazene moieties give polymers which are very stable. A hexafunctional oligomer was synthesized. The resultant liquid had a viscosity far below the 40 to 50 poises needed in an Intaglio ink resin or the 100 to 200 poises needed in a resin which can be diluted. A green ink was made from the phosphazene resin. Both the resin and the ink were easily water dispersible and also dispersed the pigments and extenders in the ink without the aid of a dispersing agent. The water-dispersion of the ink did not foam appreciably, as expected for a resin based on polyethylene oxide. The ink cured very slowly, needing some 30 megarads of electrons to become non-tacky to the touch. The cured ink was very resistant to prolonged soaking (several months) in water, toluene, and acetone. Because of the slowness of the reaction, the several steps required for the reaction sequence, the low viscosity of the product, and the slow cure of the resulting resin, the phosphazene approach was abandoned.

A comb oligomer was synthesized with polyethylene oxide arms terminated with acrylate groups. A mercaptan transfer agent was used to stop the polymerization of the backbone at about the 5-mer level. This gave a material with a polymeric backbone and long arms of polyethylene oxide terminated with alcohol groups. The material was then acrylated using acryloyl chloride. Unfortunately, it proved impossible to synthesize a sufficiently viscous resin. Attempts to use less transfer agent to give a longer backbone invariably produced a gel. The problem appeared to be a significant amount of difunctional material in the parent monomer. The acrylated resins were among the best for producing stable dispersions in water.

The reaction between alcohol and isocyanate groups is a simple one-step process which gives resins of the urethane type. These resins should be more viscous than the resins previously discussed, because the urethane linkage is known to be "stiff". Several isocyantes were tried. Among the more successful from the point of water dispersibility were hexamethylene di-isocyanate (HMDI) and a much more viscous material formed from a high temperature reaction between HMDI and water. The pattern which emerged was that water dispersibility and satisfactory viscosities could be achieved, and the resins dispersed the pigments well. The cure speed in the electron beam was reasonably good. Compared with other types of resin developed for other applications, the resins cure well and quickly. Cure in 2 megarads of exposure to the electron beam is required. Much higher exposures, in excess of about 5 megarads, seriously weaken the paper on which the ink is printed. The interplay between cure speed and stabilization of the resin using various stabilizers is now being investigated. The resin and ink films are elastomeric, and are slightly "tacky" in the cured state. Efforts are underway to reduce this tackiness and to improve the mechanical properties of the film.

Finally siloxanes were prepared through a condensation reaction between silicon tetrachloride and hydroxy groups. Although siloxanes are expected to be less viscous than urethanes, they are in general more highly functional and should cure quickly. The condensation products of polyurethanes and siloxanes differ in the hydrophobic residues joining the hydrophilic segments. The siloxane residue involves a silicon atom having a molecular weight of 28 and a functionality of 4. The urethane resins have molecular weights above 100 and functionalities of 3. Thus, for condensation products of similar type, the siloxanes have much lower hydrophobic content and therefore much greater water dispersibility. On the other hand, polyurethanes have much higher glass transition temperatures than siloxanes. The results are much higher viscosities for the polyurethanes. The siloxanes were very slow to cure in the electron beam, being only poorly cured with 5 megarads exposure. The probable cause is reduced content of the curable groups. The resins had a noticeable odor of monomer acid, probably released through transesterification.

In summary, the phosphazene resins and the siloxane resins have excellent water dispersibility but do not cure rapidly enough. The comb pre-polymers also have good water dispersibility but are not viscous enough because long molecules could not be synthesized before the system gelled. The urethane systems have good viscosities, good dispersibility in water, good dispersibility of the pigments and extenders, and adequate cure speed, even when stabilized against premature gelling. The resultant films are elastomeric.

Analysis of Structure in Polymers and Their Composites

W. L. Wu, B. J. Bauer, D. L. Hunston, H.G. Waddill[1], J. Prahinski,
J. T. Fossett, W. Su

[1] Texaco Chemical Company, Austin, TX

The determination of structure in thermoset resins during and after the curing process is a vital step in relating processing and formulation parameters to performance. During the past year, the work has used neutron scattering as a technique to characterize this structure, and some of the results of this work will be described in this section.

Network Formation of Thermosetting Polymers

The process of crosslinking long chain molecules in bulk samples has been simulated successfully up to the gelation point by the classical theory of Flory & Stockmayer (F-S). Their model is equivalent to a Bethe tree in which no closed loops are allowed. On the other hand, the results of percolation models which do allow for closed loops have been applied successfully in the crosslinking of many systems e.g. silica gel and colloidal particles. It is the goal of the work here to determine which model best describes the cure of thermoset polymers. Intuitively, one expects that the percolation model will prevail due to the size of the thermoset monomers. However, there is an obvious difference between the percolation model and the cure of a thermoset; the reactive end groups in the monomer chain are separated by many bonds while the joining reactions can involve only one bond or in the case of a crosslinking agent many bonds. As a result the length scales can be quite different. In most percolation models on the other hand, the length scales are the same. It is, therefore, of interest to determine whether either of these two models will adequately describe thermosets crosslinking throughout the whole curing process.

Experimental Characterization of Network Formation

Epoxy was chosen as the model system for thermosets, and all the cures were conducted in the bulk state rather than solutions. More specifically, diglycidal ether of Bisphenol A (DGEBA) was cured with di- and tri amines connected with polypropylene chains (Jeffamine D-230 & T-403 respectively). All the cures were conducted at 60°C for the early stages of the reaction followed by a reduction to 23°C as the gel point was approached. The reason for lowering the cure temperature in the later stages was to obtain samples with small degrees of undercure. The extent of cure was monitored by both infrared spectroscopy (IR) and viscosity. As the cure proceeded, specimens of different degrees of cure were removed from the reaction bath and dissolved in deuterated THF. For each specimen, solutions at 3 to 5 different concentrations were prepared; the lowest concentration was in the range of .2% by volume. All of these solutions were kept at -5 C throughout the remainder of experiment, and no further cure was detected in any of the solutions. Small angle neutron scattering (SANS) results for these solutions were extrapolated to zero angle and zero polymer concentration to obtain the values of molecular weight (M_w) and radius of gyration (R_g) of the crosslinked polymer chains at various degree of cure.

Since all the scattering measurements were carried out in solution, the excluded volume effect must be included in the data interpretation. Furthermore, the system involved polydispersity in that the crosslinked molecules had a distribution of molecular weights. Consequently, scattering intensity, I, would not be expected to exhibit a simple fractal type as exemplified by the following relation

$$I(q) \propto q^{-D} \qquad (1)$$

where q is the magnitude of the scattering vector and D is the mass fractal dimension by which the values of M_w and R_g are related through the simple relation $M_w \propto R_g{}^D$. After taking into account both the polydispersity and the excluded volume effects, the effective value for D is 1.64 for the percolation model and 1.0 for the F-S model.

The results for systems of the epoxy cured with the di-amines indicate that the value for the exponent D is 1.15 which is close to what predicted by the F-S model. This is surprising because the monomer sizes of the epoxy and the di-amine are far shorter than a long chain. Furthermore, the crosslinking reaction occurs at the chain ends rather than distributed along the chains. One plausible explanation is that the primary amine reacts much faster than the secondary amines as observed by other investigators, and hence, linear chains of significant length are formed in the beginning of the cure. The later stage of cure is therefore the crosslink of these long linear chains via the reaction of the secondary amines along the backbone chains. This second stage reaction might be expected to conform to the F-S theory.

In order to test the hypothesis mentioned above, a tri-amine was included in this study. For the tri-amine even if the primary amines react much faster than the secondary amines, a three dimensional network will be present in the initial stages. The SANS results for the T-403 cured epoxy do indeed yield a value for the exponent D, which is almost identical to that predicted by percolation theory, i.e. 1.67 from the experiments and 1.64 for the theory. To further test the percolation result, a high molecular weight specimen of tri-amine cured epoxy with a narrow size distribution of amine was prepared through a solution fractionating method. A typical fractal scattering behavior is observed in the corresponding SANS result and the fractal dimension is about 2.1. This value is close to that predicted by the percolation theory and called "animal-like" behavior.

In summary, the results indicate that the crosslinking of a thermoset in the bulk state follows the percolation process. However, in certain cases specific chemical reaction mechanism can modify the process towards what is predicted by the F-S theory.

Computer Modelling of Network Formation

To gain an in-depth understanding of the curing process of thermosets, computer simulation has been undertaken. The first step in this work is to simulate the crosslinking process of the di-amine/di-epoxy reaction in bulk. The basic idea is to group every two lattice sites into connected pairs where the two connected sites are not adjacent to each other. Hereafter the site percolation routine is executed on this non-adjacent paired lattice. These non-adjacent pairs are constructed to simulate the di-amines where the two reactive amino ends are connected by a pre-existing chain. Upon curing, these amino ends are connected by linear di-epoxy monomers which will not contribute to any additional crosslinks; hence a straight forward percolation process. To sum up, non-adjacent connectivity has been added to a typical site percolation process in order to simulate the cure of thermosets in bulk.

Some preliminary results in two-dimension are now available. The critical degree of cure or the percolation threshold, P_c at which the lattice starts to percolate, decreases upon introducing the non-adjacent connectivity. This result is totally expected since the addition of any connectivity can be considered as an increase of the monomer functionality. The cluster size still follows the scaling expression as follows:

$$N_S(P) = S^{-\tau} f[(P-P_c)S^{\sigma}] \qquad (2)$$

where τ and σ are two independent critical parameters, S is the cluster size, N_s is the number of clusters of size S. The value of τ depends strongly on the lattice size. So far the result suggests that the value of τ approaches 2.05 as the lattice size increases for examples both with and without the non-adjacent connectivity. In order to evaluate the function $f[(P-P_c)S^{\sigma}]$ in equation 2, four sets of data at different levels of undercure were analyzed. The value for σ is chosen to be 0.396 since it is a universal constant for a two dimensional lattice. It was found that these four sets of data could be scaled into a single master curve by using this value of σ. Since there are only two independent parameters in this type of percolation problem, and neither τ nor σ seems to be affected by the addition of non-adjacent connectivity, we conclude that the computer modelling is consistent with the SANS results.

Network Characteristics and Deformation Mechanisms

A set of SANS measurements was also conducted on fully cured bulk epoxy samples after they were swollen in deuterated THF. The results indicate that in the fully cured epoxies, the networks were not as homogeneous as an ideal polymer solution, however, the correlation length of the heterogeneity for the majority of networks is about 10 A. This finding in addition to the results presented above for the curing process are inconsistent with structure models that invoke some degree of gross heterogeneity such as nodules.

Another motivation for carrying out the study on the network formation is to unravel the deformation mechanism of epoxies for large strain amplitudes. As reported in the previous annual report, the average distance between crosslinks remained almost the same as that in the undeformed state while the sample underwent deformations of 35% or more. A chain unfolding mechanism was proposed to accommodate the observation. However, such a mechanism is only plausible if the spatial neighbors of the network are not highly entangled. The network studies conducted here served to clarify this issue since the results suggested that the network is not highly entangled.

Performance of Polymers and Their Composites

D. L. Hunston, G. W. Bullman, E. Passaglia, A. Lee, G. B. McKenna,
W. D. Bascom,[1], S. S. Wang,[2] and A. J. Kinloch[3]

[1]University of Utah, Salt Lake City, Utah
[2]University of Illinois, Urbana, Illinois
[3]Imperial College, London, England

Development of test methods and reference data for the measurement of performance properties is the focus of this subtask. This year, the subtask dealt with delamination, adhesive bond failure, and physical aging of crosslinked networks.

Delamination

Composite delamination (the growth of cracks between layers of fibers either in the polymer that holds the fibers together or at the polymer-fiber interface) can grow from impact damage and substantially reduce the mechanical performance of a composite, particularly in compression. Improving delamination resistance requires a better understanding of the failure processes involved and the factors that influence them. Previous work in the Composites Group has established the influence of matrix resin toughness on mode I interlaminar fracture behavior in the composite. Other variables such as fiber-matrix adhesion have also been identified in this program. During the last year the number of composite systems evaluated has been extended to 35, and the results, which continue to support the conclusions of the previous work, are covered in a recent publication (Proc. AUTOCOM'87, SME, 1987).

The studies have also been extended to include characterization of the fracture surfaces in an effort to gain more insight into the failure mechanisms. With the exception of polyetheretherketone (PEEK) composites all of the samples exhibited stable crack growth (i.e. slow crack propagation driven by the motion of the test machine) when tested in constant crosshead speed experiments. In these studies the crack was propagated slowly through about 80% of the sample, and then the specimen was rapidly split apart thus producing a region at the end of each sample where failure was by rapid crack growth. With brittle polymers the appearance of the fracture surface on the composite did not change markedly with this variation in crack velocity. For tough polymers, on the other hand, the surface was whitened in the region of slow crack growth, while the original dark color was retained in the region of rapid crack growth. Examination of the fracture surfaces with a scanning electron microscope indicated that the stress whitening was associated with surface roughness, microvoids, or other features created by deformation of the resin. This deformation was much greater when slow crack growth provided time for the yielding and plastic flow to occur. The much more limited yielding in the brittle resins explains why a large rate effect was not observed in these specimens.

The effects were studied further by subjecting the fractured samples to heat treatments above the glass transition temperature, T_g, of the matrix. Plasticly deformed regions on the fracture surface were observed both before and after the heat treatment with the scanning electron microscope. A surprising large degree of recovery was observed in the deformation of the matrix after the heat treatment. A similar effect was seen macroscopically. Even after only 30 minutes above T_g, all of the stress whitening had disappeared. This effect is not restricted just to composites but can also be seen in corresponding bulk resin specimens.

Another example of this effect can be observed for the fracture surfaces of PEEK composites. This particular material exhibited an unusual crack growth pattern in that alternating regions of stable (slow) and unstable (fast) crack growth were produced in constant crosshead speed experiments (for the conditions used here). The result was an alternating pattern of light and dark bands on the fracture surface corresponding to the slow and fast crack growth regions. What makes the PEEK composites particularly interesting is that since the melting temperature for the crystalline regions, T_m, is much higher than the T_g, the heat treatment can be performed at an intermediate temperature (for PEEK T_g is about 148 C while T_m is about 320 C). Surprisingly, most of the stress whitening remained even after 3 days at 200°C. The heat treatment was continued at 400°C for 8 hours, and at this point the stress whitening disappeared almost completely. This observation suggests that crystallinity acts to lock the deformation in so that only temperatures above the melting point make major recovery possible.

Adhesive Bond Failure

Joining of composites is a major area of concern, and adhesive bonding offers many potential advantages in this connection. To take full advantage of this opportunity, however, a better understanding of the failure behavior of bonded joints is needed. To address this problem, studies in the past year have used movies to examine the region at the tip of a precrack in the adhesive bond while the specimen is loaded to failure. The adhesive employed was an elastomer-modified epoxy which models the behavior of more complex commercial formulations. By using the stress whitening that occurs to characterize the crack-tip deformation zone, the movies demonstrated that the size of the zone at failure in an adhesive bond changed with alterations in the bond thickness. Moreover these changes were shown to correlate with the measured fracture energies. In thick bonds the zone size (volume) and fracture behavior were similar to those found in bulk samples. As the bond thickness was decreased, the zone size at failure grew by extending further down the bond line. The fracture energy exhibited a corresponding increase. Eventually, a point was reached where further decreases in bond thickness cause the fracture energy to decrease. This change occurred at approximately the point where the height of the deformation zone was equal to the bond thickness. Thus further decrease in thickness might be expected to reduce the zone size by constraining the zone height. Qualitative explanations for these effects were developed. The movies also demonstrated that the pattern of growth for the deformation zone and the presence or absence of subcritical crack growth depended on the bond thickness. Finite element models were used to predict the growth of the deformation zone in thick bonds, and the resulting correlation was quite good (see Fig. 3). Continued studies based on this approach will lead to a more complete understanding of adhesive bond failure and the factors which control it.

Physical Aging

With composite materials and structural polymers being used in an increasing number of applications, concern regarding long term behavior becomes important. One interesting aspect of long term behavior for structural polymers is their tendency to change with time do to the physical aging phenomenon. If these materials are to be used effectively, it is important to develop a better understanding of this effect and the material and structural characteristics which determine the sensitivity to physical aging. In this study the role of crosslink density is being investigated. Crosslink density has a strong influence on the glass transition temperature, T_g, and the changes in thermodynamic properties that occur at T_g, specifically the changes in specific heat, ΔC_p, and in volume thermal expansion coefficient, $\Delta\alpha$. This program seeks to determine what effects these parameters have on physical aging behavior.

Epoxy (Diglycidyl ether of bisphenol A, DEGBA) was chosen as the model system for the study, and the crosslink density was varied by using three amine crosslinkers of different molecular weight (amine terminated poly(propylene oxide)). The T_g's of the resulting networks ranged from 87°C to 42°C as measured by DSC. The curing and structure of these systems has been well characterized in previous studies at NBS.

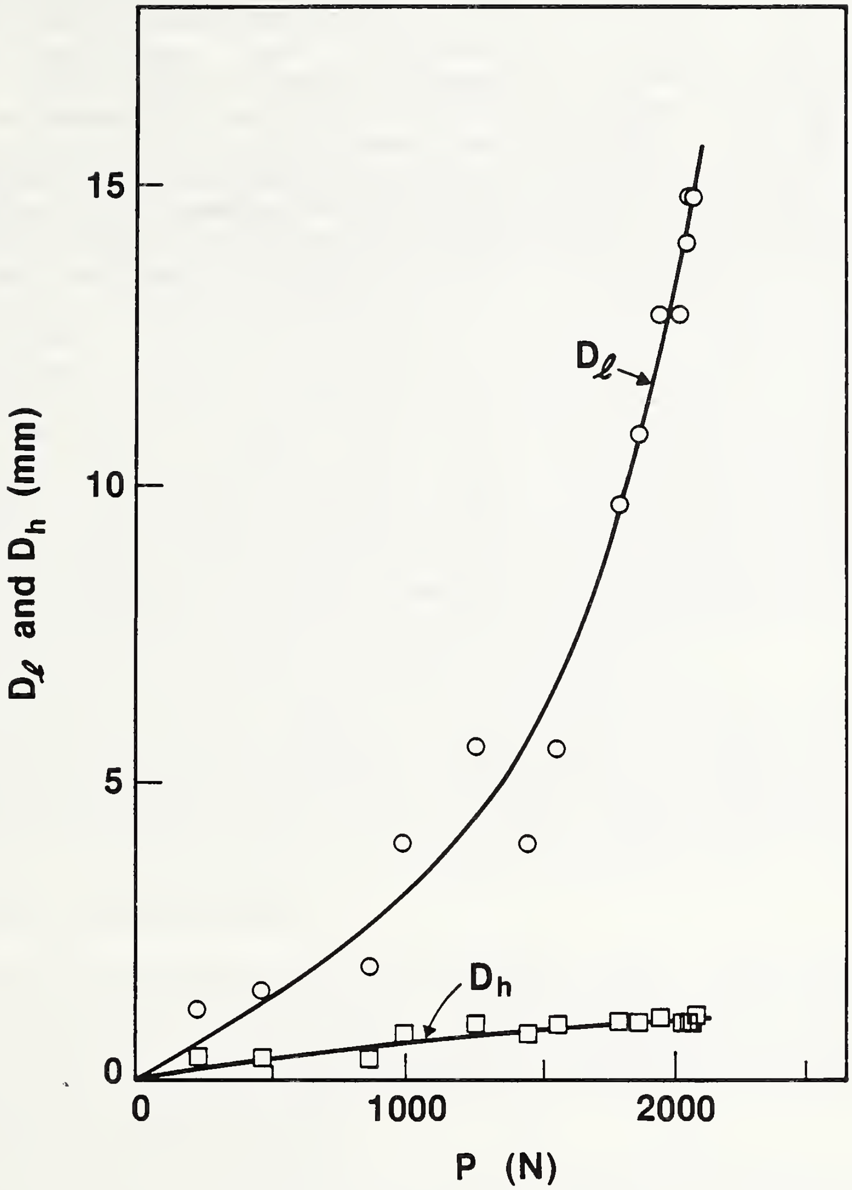


Figure 3: Growth of the crack-tip deformation zone length, D_l, and height, D_h, as a function of load, P. Curves are finite element predictions while points are measurements from the movie.

Aging behavior was investigated at constant temperatures below T_g using small-strain stress-relaxation measurements in uniaxial extension after quenching from above T_g. As expected, the relaxation modulus of the network increased as the material aged, and the stress relaxation curves at various aging times could be superimposed with aging time shift factors, a_{te}. At temperatures about 10°C below T_g it was possible to obtain aging times sufficiently long for the sample to reach equilibrium, and thereafter no further aging occurred. Although the three networks tested had different T_g's and different crosslink densities, all three were found to have very similar values for ΔC_p. Moreover, no significant differences in the physical aging behavior were observed for the three networks. Ongoing studies are utilizing stiffer epoxies such as tetraglycidylmethylene dianiline, TGMDA, and other polyfunctional aryl epoxies which are expected to show differences in ΔC_p as well as T_g so the effect of this thermodynamic parameter can be examined.

POLYMER BLENDS

Polymer properties can be improved and tailored for specific applications through various blending processes. The current and potential technological importance of polymer blends is remarkable and is clearly evidenced by their ubiquitous presence in consumer products.

A similar way that stainless steels which are alloys of iron, chromium, and nickel make metal more resistant to corrosion, polymer blends which are a mixture of two or more polymers form plastic alloys with new properties. Mechanical properties, flame retardance, processability, as well as many other properties can be improved by blending. The blending of low cost polymers into new alloys is a relatively inexpensive way to produce materials with new properties, but most polymers fail to form a homogeneous phase during the blending process. Although miscibility in polymer blends is neither an absolute requirement nor always desirable, nevertheless, the phase separated alloy often gives inferior properties if the structure, morphology and interfacial adhesion are not controlled. On the other hand, an improvement of properties by an order of magnitude, such as the impact resistance, can be achieved through the synergistic effect of a well controlled phase separated alloying process. Two major factors leading to an understanding of how to produce desirable heterogeneous blends are: (1) a better knowledge of the fundamental factors that control the 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.

Small angle neutron scattering (SANS) and time resolved temperature-jump light scattering (TJLS), are basic techniques being used to obtain information on phase diagrams and demixing kinetics. In addition to these two techniques, Forced Rayleigh Scattering (FRS), small angle X-ray scattering (SAXS) and electron and optical microscopy are also used in polymer-blend studies.

FY 87 Significant Accomplishments

- The Cahn-Hilliard-Cook equation has for the first time been proven to be quantitatively correct. The equation was applied to spinodal decomposition of a polystyrene/poly(vinylmethylether) blend system. Data verifying its accuracy came from time resolved temperature jump and reverse quench light scattering techniques, and from a structure factor measured by a SANS experiment.

- The interdiffusion coefficient, D, of a polymer blend was shown to be a continuous function of temperature at and around a compatible-incompatible phase boundary. The value of D, which changes sign at the boundary, leads to derived mobilities that have an Arrhenius temperature dependence.

- A single phase interpenetrating network was formed from linear poly(vinylmethylether). Such single phase interpenetrating networks are rare because the normal statistical spatial variations in numbers of crosslinks usually cause phase separation.

- Entropy theory was successfully applied to glass formation in polymeric ring systems. The glass formation temperatures increase sharply with decrease in molecular weight for these ring polymers, while the opposite is true for the much more common linear polymers. The theory was shown to predict both results.

Experimental

C. C. Han, R. M. Briber, B. J. Bauer, D. L. VanderHart, J. Clark,
Y. Matsushita[1], T. Sato[2], Q. Tran-Cong[3], P. Sung[4], S. Sakurai[5], M. He[6]

[1]Nagoya University, [2]Osaka University, [3]Kyoto Institute of Technology,
[4]FDA, [5]Kyoto University, [6]East China University of Chemical Engineering

Polymers Bearing Intramolecular Photodimerizable Probes for Mass Diffusion Measurements by the Forced Rayleigh Scattering Technique: Synthesis and Characterization

A new photochromic probe, 9-bis anthryl methyl ether (BAME) derivative, was synthesized and introduced as an effective probe for the Forced Rayleigh Scattering (FRS) measurement. It is shown that BAME and polystyrene labeled with BAME exhibit a large change in refractive index under irradiation of UV light (363.8nm). The self-diffusion of BAME and polystyrene labeled with BAME (PSA) were measured in various solvents. Results for PSA in good, marginal and poor solvents are consistent with those obtained from quasi-elastic light scattering (QELS). Other than the exception of using BAME as a probe in fluorescence quenching solvents, our results indicate that BAME is a very effective probe. It overcomes many difficulties which are present in the use of other photochromic probes for the mass diffusion measurements of FRS.

Dynamics of Concentration Fluctuation in a Polymer Blend on Both Sides of the Phase Boundary

The dynamics of concentration fluctuation in a deuterated polystyrene/poly(vinylmethylether) blend system has been studied by the temperature jump and also by the reverse quench light scattering techniques. The growth or decay rate R(q) in Cahn-Hilliard-Cook's equation is almost proportional to the square of scattering wave vector. This indicates that the interfacial free energy contribution to the concentration fluctuation dynamics in the wavelength range examined is very small. The interdiffusion coefficient D which has been obtained as a function of temperature, is continuous at the phase diagram boundary. The mobility M, which can be extracted from D by combining the results of both statics and kinetics has an Arrhenius type of temperature dependence on both sides of the phase boundary.

Phase Contrast Matching in Lamellar Structures Composed of Mixtures of Labeled and Unlabeled Block Copolymer for Small-Angle Neutron Scattering

To extract the single-chain scattering function of a polystyrene block chain in lamellar structures of styrene-2-vinylpyridine diblock copolymers, the method of "phase contrast matching" was studied for small-angle neutron scattering from blends of the deuterium-labeled and unlabeled block copolymers. The phase contrast matching is successfully applied for the samples with the lower molecular weights (3.4×10^4 and 9.2×10^4 for the labeled portions) but not for the sample with the highest molecular weight (16.2×10^4) and not for samples with partially deuterated blocks. The cause of the mismatching is attributed to non-uniform distribution of the deuterated species along the direction perpendicular to the lamellae due to difference in chain lengths of the labeled and unlabeled blocks rather than to the incompatibility between hydrogenerated and deuterated polystyrenes.

Structure and Morphology of MDI/BDO Based Polyurethanes

Polyurethanes are random block copolymers consisting of alternating sequences of hard and soft segments along the chain. The hard segment is based on diphenyl methane diisocyanate with butanediol (MDI/BDO) and the soft segment is based on polytetramethylene oxide. The mechanical properties are believed to be strongly influenced by the size and shape of the microphase separated hard segment domains. We have been studying the morphology of the hard segment domains by wide and small angle x-ray scattering (WAXS and SAXS) and how it is influenced by temperature and deformation. WAXS shows that the hard segment repeat unit undergoes conformational changes with deformation with the hard segment repeat length changing continuously with deformation.

SAXS indicates that the morphology of the hard segment domains changes extensively as the temperature of the sample is increased. The long period and scattered intensity increases with increasing temperature. SAXS will also be used to study the effect of deformation on the morphology in conjunction with the mechanical properties.

High Use Temperature Polymer Blends

Polymer blends of polybenzimidazole and polyetherimide have been made by solution casting. Differential scanning calorimetery, SAXS, NMR and transmission electron microscopy indicate that the blends are homogeneous when cast from a common solvent (DMF). Heating above the glass transition temperature of the blend induces phase separation. The blends of these polymers show a number of desirable properties relative to the pure components including enhanced solvent resistance and lessened moisture uptake.

SANS of Single Phase Interpenetrating Polymer Networks

Single phase interpenetrating polymer networks (IPN) synthesized from linear polyvinylmethylether (PVME) and crosslinked deuterated polystyrene (PSD) have been studied by small angle neutron scattering (SANS). Uncrosslinked blends of these materials are compatible at room temperature and will phase separate on heating (at about 150°C). Compatible IPNs can be made if the crosslink density is not too large. At the temperature of polymerization, (70° C) the IPNs phase separate at crosslink densities 1% or greater of PSD. Upon heating the single phase IPNs the SANS intensity at zero angle, $S(0)$, increases but not as quickly as in the linear blends. This indicates that in the compatible IPNs the spinodal temperature is increased relative to the linear blend. In addition, the plot of $1/S(0)$ versus $1/T$ (used to determine the spinodal temperature) is not linear indicating that classical mean field exponents do not apply. The effect of deformation on the phase separation behavior was also studied. Deformation caused the spinodal temperature in the direction parallel to the deformation to shift to a lower temperature relative to the spinodal temperature perpendicular to the deformation.

SANS of Crosslinked Polymer Blends

Small angle neutron scattering (SANS) has been used to study the phase separation behavior of polyvinylmethylether (PVME) deuterated polystyrene (PSD) blends crosslinked by gamma ray irradiation. As predicted by de Gennes (1), the scattering function shows a peak at a non-zero q vector although the position of the peak appears to be at a q vector smaller than predicted. Also, the data indicate that the effect of concentration fluctuations that are present at the temperature of crosslinking (45° C), which give rise to nonzero scattering at q=0 needs to be included in the theory. Plotting the inverse peak intensity versus 1/T to determine the spinodal temperature demonstrates that the phase transition temperature increases rapidly with increasing crosslink density.

1. de Gennes, P. G., J. Physique Lett., 40, L-69(1979)

Gas Transmission Measurements

Bill Welsh, an Industrial Research Associate from Armstrong World Industries, has been performing measurements of permeabilities of gases important in the production of foamed plastic materials. These measurements indicate that appreciable releases of these gases can be expected because of the high permeability of materials to the gases. Diffusion coefficients are low, but the solubilities of the gases in the tested polymers are quite high.

Theory

E. A. Di Marzio

Superlattice Structure of Crystal Growth

The thermodynamics of inhomogeneously stressed systems is being investigated. An application concerns the growth of a thin plate-like crystal (that normally prefers to grow in a plane) onto the surface of a sphere. We have estimated the reduction in supercooling due to stress build-up in the crystal. The accumulated stress also forces a transition from spherical symmetry to cylindrical symmetry resulting in tubules (scrolled lamellae).

Molecular Conformation of Star Polymers and Free Polymers Under Constraint

The dimensions of a star molecule are easily estimated by a simple modification of the Flory method. The results are that the square of the radius of gyration is proportional to the 1.2 power of molecular weight and to the 0.40 power of functionality. This is to be compared to the scaling analysis of Daoud who obtains 1.18 instead of 1.2 and 0.41 instead of 0.40. Monte Carlo results with many hours on a Cray computer cannot distinguish between these two sets of predictions.

The dimensions of a free polymer molecule imbedded in a field of oriented polymers or rod-like molecules is not yet understood. Recent neutron scattering results show that the free polymers are elongated much more than predicted by theory. A new theory is considered which takes explicit account of the fact that polymer bonds (of the free polymer) prefer to lie along the direction of the oriented molecules. We have calculated the probability of bond orientation of the free polymer and find that it is no longer isotropic, so that the free polymer is lined up in the direction of stretch even though it is not tied to the network.

SAXS and Pole Figure Facilities

J. D. Barnes and F. I. Mopsik

Digital Camera for Small-Angle X-Ray Scattering

The SAXS facility is essentially fully available for users. Results have been obtained from SBS triblock copolymers (U Mass), polyurethanes (NBS for FDA), and "discotic" molecular crystals (Georgetown Univ.) The software for driving the camera and displaying the data has evolved to the point where new users can become comfortable with the instrument after a relative minimum of training.

The data acquisition software permits the user to schedule a sequence of data acquisition tasks and leave the camera to unattended operation. Automatic interlock systems are provided to protect the detector from excessive beam flux, shut down the vacuum system in the event of a failure, etc. The computer that acquires the image histogram is networked to the watchdog computer for the beam line in order to provide control of the exposure parameters, to download archival information such as exposure time and monitor count, and to drive the positioning motors for the x-ray optics.

Software for applying all needed corrections has been implemented. The data can be displayed in the form of false-color video images or line graphs. All data are properly normalized to time or monitor count. They can then be either circular or sector averaged according to the user's needs for further analysis.

Interest From Outside Users

Poster papers describing the facility were presented at meetings of the materials Research Society and the American Physical Society. The NBS public information office placed descriptions in a wide range of print media. The response has been good as a number of workers from other NBS divisions, government agencies, industry, and academia have expressed interest in using the SAXS camera for work on materials of interest to them. We expect these contacts to evolve into a number of requests for Industrial Research Associateships and proprietary use.

X-Ray Pole Figure Facility

An Industrial Research Associateship has been established with Dr. Charlotte Chen-Tsai as the principle investigator from ALCOA. This work is aimed at evaluating the effects of processing under conditions of solid-state extrusion on the orientation texture of sheets and films of engineering plastics.

DENTAL AND MEDICAL MATERIALS

The objective of this research 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 or therapeutic equipment, 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 via utilization of adhesives and durable space occupying materials for use in cavity preparations. These include new composite resin formulations with reduced polymerization shrinkage and more resistance to attack by oral fluids as well as macroscopic bulky space fillers bonded to cavity walls. Strong, more durable, versatile dental cements are also explored. 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 is also under investigation.

Theoretical and experimental studies of stresses within bonded dental systems are explored with the objectives of defining the most compatible material-property combinations and geometric designs for porcelain-to-metal, tooth-to-resin, resin-to-filler bonding and so forth. Characterization of materials by Weibull statistics is being employed with a view toward using those parameters 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 studied with a view toward improved alloys and processing methods.

FY 87 Significant Accomplishments

- A new adhesive which adheres to both hard and soft tissues was formulated. Its basic component is an acrylic backbone with pendent isocyanate groups. The new adhesive was shown to produce bonds equivalent in strength to bone.

- The use of α-methylene-C-butyrolactone in polymerizable dental resins was found to enhance the degree of cure of the hardened polymer. This and other advantages make this monomer a potential replacement for methyl methacrylate in dental composites, denture bases, bone-cements and related biomedical applications.

- A possible precursor to pathological calcification has been identified. Octacalcium phosphate was found involved in calcium phosphate precipitates in ultrafiltered serum. Knowledge of the pathological calcification mechanism may lead to treatments to inhibit vascular and other types of unwanted calcification.

- A variety of dental composites were characterized by a new technique for their susceptibility to marginal failures. The method uses Weibull statistics to evaluate the results of failure tests on specially designed fracture specimens.

Dental Composite and Cement Sealant and Adhesion Chemistry

J. M. Antonucci, R. L. Blosser[1], R. L. Bowen[1], G. M. Brauer, E. E. Cobb[2], F. C. Eichmiller[1], A. D. Johnston[1], R. W. Penn, N. W. Rupp[1], J. W. Stansbury, A. Sugawara[3] and S. Venz[4]

[1]American Dental Association Health Foundation, Paffenbarger Research Center, (ADAHF/PRC) at NBS
[2]Dental School, Georgetown University, Washington, DC
[3]Nihon University, Tokyo, Japan
[4]Dentsply International, Milford, DE

A potential problem that may affect the clinical performance of resin based dental composites, which are polymerized under ambient conditions (20-37°C), is their incomplete conversion (40-70%). The presence of mainly pendant vinyl groups and minor amounts of "free" monomers or oligomers has a plasticizing effect on composites, predisposing them to other adverse effects which compromise the durability of restorative materials. The use of minor amounts of a highly reactive monomer that is also a good solvent for the developing polymeric matrix is a promising approach to reducing residual unsaturation of dental sealants and composites. To test this hypothesis, the highly reactive vinyl lactone, α-methylene-γ-butyrolactone (MBL), was added to several typical dental resin formulations. The polymerized resins showed enhanced degrees of cure and mechanical properties compared to controls without MBL. This interesting monomer, which is a cyclic analog of methyl methacrylate, has many unique chemical and physical properties that suggest its use in denture base, bone cement and other biomaterial applications.

Another approach towards improving the conversion of resin based dental materials is by optimizing the efficiency of their initiator system. Tertiary amines are widely used as polymerization accelerators in both chemically and photochemically activated dental resin systems. In chemical cures, tertiary aromatic amines and benzoyl peroxide are thought to form unstable complexes which then generate initiating radicals. Visible light polymerization involves formation an exciplex between a tertiary amine and an excited α-diketone such as camphorquinone which then rapidly decomposes to initiating radicals. In both these processes the unshared electron pair on the nitrogen of the tertiary amine is deemed essential to the efficacy of the initiator system. Certain amine derivatives, e.g. salts of strong acids, such as p-toluene sulfonic acid and BF_3, were prepared, which presumably tie up the "free" electron pair of these amine activators. Surprisingly many of these amine derivatives still function as free radical polymerization accelerators, yielding composites with excellent mechanical properties and esthetics. The possibility of the strong acid complex, e.g. $R_3N \bullet BF_3$, having potential for use in dual cures, i.e. free radical/ionic polymerizations, is under investigation. In addition, a structure-property study of various types of photoaccelerators for camphorquinone also is under investigation. Preliminary results indicate that sterically unhindered tertiary aromatic amines with maximal numbers of α-hydrogens give higher degrees of cure than similar tertiary aliphatic amines. Generally, however, tertiary aliphatic amines yield composites with better color stabilities. A sterically hindered tertiary aliphatic amine (a HALS type amine) gave composites with relatively high degrees of cures having both excellent esthetics and color stabilities.

Several glass formulations were evaluated for use as glass inserts for composite restorations. Properties of thermal expansion, light transmittance, and fracture strength were evaluated along with the effects of inserts on polymerization shrinkage. The incorporation of glass inserts in composite restorations may prove to be an effective method of improving the overall performance of dental restorations. Current work is focused on the application of microcrystalline glass ceramics which have thermal and physical properties which are much more desirable for insert applications.

The use of monomers that undergo volumetric expansion on polymerization offers one method to modify the deleterious effect of polymerization shrinkage. A series of spiro orthocarbonate monomers capable of free radical polymerization with double ring-opening to achieve an expansion in volume was investigated. The monomers were homopolymerized and the degree of ring-opening and the polymerization expansion were determined. In copolymerization studies with conventional monomers, the relative reactivity and degree of ring-opening of selected spiro-monomers was also evaluated. The ring-opening polymerization efficiency of the various spiro-monomers was then related to this degree and pattern of ring substitution as well as ring size.

Based on the analysis, two compounds were found to be potentially useful in dental polymer systems: 2-methylene-8-(5'-norbornen-2yl)-1,4,6,10-tetraoxaspiro[4.5]decane and 2-methylene-8,8-dimethyl-1,4,6,10-tetraoxaspiro[4.5]decane.

Wear, Durability, Clinical Studies and Related Properties of Dental Composites, Amalgams, Cements and Glass-Ionomer Cements

J. M. Antonucci, R. L. Bowen[1], W. de Rijk[2], F. C. Eichmiller[1],
A. A. Giuseppetti[1], J. E. McKinney, N. E. Rupp[1], R. W. Penn, and R. W. Waterstrat[1]

[1] ADAHF/PRC
[2] Dental School, University of Maryland, Baltimore, MD and NBS

The feasibility of developing dental-dual cure hybrid cement-composites (HCC's) from polyelectrolyte-based cements, e.g. glass-ionomer cements, using compatible vinyl monomers and free radical initiator systems was demonstrated. The resulting resin-modified cements or HCC's exhibited a significant improvement in diametral-tensile strength, but somewhat lower compressive strength, microhardness, and wear resistance. Unlike conventional glass-ionomer cements or other cements (metal modified glass-ionomer cements), HCC's displayed a markedly reduced incidence of catastrophic failure during wear testing. There was also improved chemical resistance to degradation resulting from exposure to acid environments. During the dual-setting process, HCC's proved to be less sensitive to excessive hydration and, after curing, less subject to dehydration than glass-ionomer cements. When used as the base material for indirectly bonding resin-based composites to dentin (via the glass-ionomer cement-composite laminate, or sandwich, technique) HCC's do not require prior etching or the use of intermediary bonding agents to achieve a satisfactory seal against microleakage.

An in vitro performance evaluation was completed on the second version of an experimental dental composite restorative employing a flexible resin which comprised a thermosetting poly(fluoromethacrylate), (PFMA), α-methylene-γ-butyrolactone, and a crosslinking diluent. PFMA was selected because of 1) its low solubility-parameter value, which is below that for most liquids found in the intraoral environment, and 2) its low monomeric viscosity, which makes possible a high degree of cure after gelation. The softening resistance on exposure to organic solvents (food simulators) was better than that for any other composite so far tested including BIS-GMA based composites currently used in practice.

A profilometer system has been designed for measuring wear of dental composites. The micropositioner and the digital control circuits for the profilometer have been completed and are functioning.

The first phase of human clinical trials using a ferric oxalate dentin bonding system has been completed. This trial involved placement of composite restorations in human bicuspid teeth which were extracted for orthodontal treatment. Pulpal evaluation of these teeth indicated no adverse reaction to the ferric oxalate, NPG, PMDM bonding system in human subjects.

A new activity is the determination of the effects of metallic dental restorations on electron production and scatter in patients receiving head and neck radiation therapy. Measurements are being made of field enhancement adjacent to metallic restorations to characterize this effect for different restoration types and therapy energy levels. Field enhancement experienced adjacent to large metallic restorations has been associated with localized mucositis and glossitis lesions. A simple method of shielding the tongue and cheek utilizing addition silicone impression materials has been developed and proves to be effective in preventing these lesions. Work will continue on exploring possible shielding applications of this material by reformulating with different fillers of varying radiodensities.

Calcium Phosphate Chemistry, Biochemistry, Structure and Clinical Implications

W. E. Brown[1], C. M. Carey[1], L. C. Chow[1], N. Eidelman[1], E. D. Eanes[2],
B. O. Fowler[2], T. M. Gregory[1], A. W. Hailer[2], B. R. Heywood, M. Mathew[1],
D. N. Misra[1], B. A. Sieck[1], S. Takagi[1], B. Tomazic[1], M. S. Tung[1], and
G. L. Vogel[1]

[1] ADAHF/PRC
[2] National Institute of Dental Research (NIDR) at NBS

The roles of octacalcium phosphate (OCP) in the formation and on the properties of hydroxyapatite (OHAP), the major component of tooth and bone mineral were investigated. The effects of small organic molecules on the conversion of OCP to OHAP and possible incorporation into OCP were also studied.

Investigation of de- and remineralization of dental specimens using Synchrotron radiation and tunable x-ray magnifier at the NBS Material Science beamline x-23A, National Synchrotron Light Source (NSLS) at Brookhaven are continuing. Preliminary analysis show an expected variation in microstructural details as a function of the wavelength used. Critical evaluation of these results are in progress.

The effects of oral rinses on enamel fluoride (F) uptake, caries, and plaque pH in rates were investigated using (1) an acidic calcium phosphate solution (CPS) saturated with dicalcium phosphate dihydrate (DCPD) and (2) a 1% fluoride solution. The groups treated with F exhibited significantly higher mean levels of enamel-bound F than the non-F groups. CPS significantly increased uptake of F by enamel when used as an adjunct to the F treatment. A strong negative correlation was observed between enamel F content and caries scores.

A better knowledge of pathological calcification mechanisms should provide a rational basis for their control. Dicalcium phosphate dihydrate (DCPD, $CaHPO_4 \bullet 2H_2O$) was used as a source of calcium and phosphate ions to investigate the mechanism of formation of more basic and more insoluble calcium phosphates in untrafiltered serum (u.f.s). Results strongly suggest that calcifications, beneficial and pathological, that take place in serum may involve OCP as a precursor, which hydrolyses in situ to a more basic apatitic product. Results also indicate that direct formation of OHAP in u.f.s. is a very slow process and may occur only rarely. The process appears to be similar in whole serum.

Microscopic and electron microprobe analyses have indicated substantial morphological and spatial heterogeneity in mineral deposits from human aortas and bioprosthetic devices implanted in experimental animals. Similarities in deposits suggest that they form by a common mechanism (e.g., OCP could be the precursor for the deposits).

It has recently been shown that a mixture of two calcium phosphate powders, one basic (tetracalcium phosphate, $Ca_4(PO_4)_2O$) and the other acidic (dicalcium phosphate dihydrate, $CaHPO_4 \bullet 2H_2O$, or anhydrous dicalcium phosphate, $CaHPO_4$), when combined with water will harden somewhat like gypsum. Results of a study point to the possibility that this calcium phosphate cement (CPC) can be used in greatly simplified endodontic procedures. CPC was examined for its ability to provide effective obturation of root canals when used as a sealer-filler combination. The good sealing ability of the CPC suggests that it may be used as a filling material without a separate sealer.

The bone mineral ratio (BMR) of trabecular to compact bone is proposed as a parameter for identification of asymptomatic population at risk for osteoporosis. The calculation indicates that, both in male and female groups, BMR is not significantly different between young and older normal subjects, i.e., age-independent, and decreases significantly for osteoporotic patients. This is indicative of preferential bone loss in trabecular bone due to osteoporosis and suggests that BMR should be a sensitive parameter for early diagnosis of osteoporosis.

An ultra micro analyses system developed in this laboratory has been employed to investigate the suitability of various types of calcium electrodes for studying mineralization potential. This study revealed that electrodes based on a "neutral ion carrier" sensor were superior in their resistance to protein artifacts. This system was also used to study plaque buffering in human dental plaque in the absence of a sugar challenge. This study demonstrated that this buffering is much different than saliva buffering and appeared unrelated to salivary access. Similarly no relationship between salivary access and potassium or fluoride concentration was found. These results indicate that the influence of saliva on human dental plaque may be much less than previously thought. Finally, the influence of membrane phenomena in ion transport through porous bulk phases was examined with an experimental model. Membrane phenomena may explain the maintenance of calcium and phosphate at nonstoichiometric ratios and at very high concentration within carious lesions and in human dental plaque. The principles enunciated as a result of this research may have important ramifications for a number of biological processes.

Results with colloidal liposome systems showed that acidic phospholipids (APL) can substantially retard membrane-centered calcium phosphate precipitations. Retardation is directly correlated with the extent to which APL polar head groups interacted with apatite surface calcium.

Transmission electron microscopic analysis revealed that the ability of phosphatidic acid (PA)-containing lipid membranes to arrest apatite growth in *in vitro* liposome suspensions resulted in part from PA binding nascent seed crystals within the interior of liposomes.

Analyses of the water components in a series of essentially stoichiometric hydroxy-apatite reference materials indicate the about one water molecule per hydroxyapatite unit cell may be structurally incorporated. The lattice positions of this water and its effects on properties of hydroxyapatite are unknown.

Dental Alloys, Ceramics, Metrology, and Analysis

J. M. Antonucci, K. Asaoka[1], R. L. Bowen[2], W. de Rijk[3], F. C. Eichmiller[2], A. A. Giuseppetti[2], R. W. Hinman[4], J. E. McKinney, O. Okuno[5], R. W. Penn, and R. W. Waterstrat[2]

[1]Tokushima University School of Dentistry, Tokushima, Japan
[2]ADAHF/PRC
[3]Dental School, University of Maryland, Baltimore, MD
[4]Naval Dental Clinic, San Diego, CA
[5]Tokyo Medical and Dental University, Tokyo, Japan

Weibull statistics offers the opportunity to more fully characterize dental material systems. The Weibull moduli and scale parameters have been determined for the fracture strength of several porcelain-fused-to-metal systems that have been modified, as well as for resins used to bond dental prosthesis. The software developed here is now in use at the dental schools of U. of MD and U. of Illinois Medical Center, Chicago. These data will be used in conjunction with finite element modeling for reliability analysis.

Dental instruments and handpieces can be degraded by autoclaving while cold liquid sterilization is often less effective. Therefore, plasma sterilization is being investigated. A cold gas plasma has been obtained in a vacuum chamber, with a microwave oven providing the RF energy sustaining the plasma.

Previous studies have shown that the setting expansion of dental investments (at the pattern site) is virtually nil. It is of interest to know what the behavior is relative to thermal expansion. High temperature strain gauges have been obtained (750°C) and a method is being developed to incorporate these strain gauges in casting investments.

The effect of dental porcelain repair procedures (reglazing) on the final strength of the porcelain is being investigated. Fracture data have been obtained and are currently being evaluated. The results are expected to shed light on the viability of this common dental laboratory practice.

A method of determining remaining dentin thickness on dental preparations has been developed and tested under clinical applications. This method utilizes the measurement of electrical impedance between the cut wall of dentin and the pulpal chamber of vital teeth. The method may prove valuable in dental material trials where specified remaining dentin thicknesses must be achieved to yield biologic compatibility data. This method could also be applied to restorative preparations where pulp exposure is a frequent risk as a measurement or warning of pulpal proximity.

A method was recently discovered for producing dimensional compensation for casting shrinkage in zirconia investment mold material. By eliminating the proprietary colloidal zirconia binder solution which had been used, and replacing it with pure water, dimensionally accurate titanium castings of good quality have been produced. Work continues on improving the casting methods in order to make them economically attractive for commercial dental laboratories.

The question of how to confidently predict the thermal compatibility of porcelain-metal systems has not been resolved. Numerous procedures have been proposed but each fails in some fundamental way for example, considering porcelain as a solid without viscous relaxation or ignoring thermal gradients during cooling etc. To overcome some of these deficiencies, a computer simulation of stress build-up in porcelain was developed. Results agree well with those published for tempered glasses. The technique will now be extended to porcelain on metal and reliability analysis performed using the Weibull parameters found for certain porcelain-metal systems as described elsewhere in this section.

The origin of failure inducing flaws in dental composites is of interest to help identify methods for strengthening composite restorations. By appropriately changing surface areas, volumes and stress distributions it is, in principle, possible to identify where failure initiates on a surface, an edge, in the bulk etc. of a composite. A study of this nature was conducted on two commercial materials. One was found sensitive to edge failures, the other was not. This suggests that some composites are clinically sensitive to finishing at margins, whereas others may not be.

A technique for characterizing the casting behavior of dental alloys has been described in previous reports. By solution of simultaneous equations the effects of different elements were quantitatively described as functions of casting and mold temperatures. A synergistic effect on the castability of beryllium and silicon was discovered for the Ni based alloys used.

Medical Materials: Improved Tissue Adhesive and Improved Surgical Bone Cement

G. M. Brauer, J. W. Stansbury, C. Lee[1], R. W. Penn and J. A. Tesk

[1] Sichuan Medical College, Chengdu, Peoples Republic of China

A biocompatible tissue adhesive for bonding to bone, teeth, and soft tissues would find many applications in orthopaedics, dentistry and surgery. More than 30 oligomers consisting of an acrylic backbone and pendant isocyanate groups ranging in concentration from 2 to 18% have been synthesized and characterized by GPC and HPLC, intrinsic viscosity, infra-red spectroscopy and titrometric procedures. These oligomers give strong, permanent bonds (that do not deteriorate in water) to glutaraldehyde pretreated bone, dentin and soft tissues. They also bond tissues to acrylic resins and composites. The biocompatibility of the oligomers and bone specimens cemented with them are being investigated by a number of academic laboratories. A patent has been applied for.

Cured specimens of radiopaque bone cements containing poly(methyl methacrylate-co-pentabromophenyl methacrylate) beads have shown radiopacity which exceeds that of commercially available radiopaque bone cement. A patent application is in progress.

OUTPUTS/INTERACTIONS

Publications

Antonucci, J. M. Resin based dental composites-an overview. Proc. of the 2nd Intl. Conf. on Polymers in Medicine, Capri, Italy, in Polymers in Medicine II, Plenum Publishing Co., E. Chiellini, et al., eds., pg 277, 1986.

Kuo, J. S.; Antonucci, J. M; Wu, W. L.; Venz, S. Evaluation of siloxane-containing dental composites. J. Dent. Res. in press.

Ubrich, J. M.; Cheikh, F. B.; Halary, J. L.; Monnerie, L.; Bauer, B. J.; Han, C. C. Molecular weight effects on the phase diagram of polystyrene poly(vinylmethyl ether) blends. Macromolecules 19: 819; 1987.

Asmussen, E.; Bowen, R. L. Adhesion to dentin mediated by gluma: effect of pretreatment with various amino acids. J. Dent. Res. 66(8): 1386; 1987.

Blosser, R. L.; Bowen, R. L. Effects of purified ferric oxalate/nitric acid solutions as a pretreatment for the ntg-gma pmdm bonding system. Dent. Matls., in press.

Bowen, R. L.; Tung, M. S.; Blosser, R. L. Dentine and enamel bonding agents. Intl. Dent. J., in press.

Chohayeb, A. A.; Bowen, R. L.; Adrian, J. Pulpal response to a dentin and enamel bonding system. Dent. Matl., in press.

Asmussen, E.; Bowen, R. L. Adhesion to dentin mediated by gluma: effect of acidic pretreatments. J. Dent. Res., in press.

Bowen, R. L. Review of the paper: bonding agents and adhesives, by R. W. Phillips, Proc. of the Intl. State of the Art Conf. on Restorative Materials, in press.

Brauer, G. M. Color changes of composites on exposure to various energy sources. J. Dent. Matl., in press.

Iizuka, H.; Brauer, G. M.; Rupp, N. W.; Ohashi, M.; Paffenbarger, G. Forces fracturing cements at die interfaces and their dependences on film thickness. Dent. Matl., in press.

Briber, R. M.; Khoury, F. A.; The phase diagram and morphology of blends of poly(vinylidene fluoride) and poly(ethyl acrylate). Polymer 28: 38; 1987.

Briber, R. M.; Sung, P. A waxs study of the deformation behavior of MDI/BDO based polyurethanes. Poly. Comm. 28: 162; 1987.

Briber, R. M. Electron microscopy of polymer blends. Proc. Electron Microscopy Society of America, 1987.

Briber, R. M. Microanalysis and electron energy loss spectroscopy of polymers. Proc. Electron Microscopy Society of America, 1987.

Briber, R. M.; Khoury, F. A. Electron energy loss spectroscopy: application to synthetic organic polymers. J. Poly. Sci. Poly. Phys. Ed., in press.

Quay, J. R.; Blackwell, J.; Briber, R. M.; Thomas, E. L. The hard segment unit for MDI-BDO-based elastomers: a combined x-ray and electron diffraction approach, in press.

Broadhurst, M. G.; Chiang, C. K.; Davis, G. T. Dielectric phantoms for electromagnetic radiation, J. Mol. Liquids 36: 47; 1987.

Broadhurst, M. G.; Chiang, C. K.; Wahlstrand, K. J.; Hill, J. M.; Dissado, L. A.; Pugh, J. The dielectric properties of biological tissue (crassula portulacea) from 10^{-2} to 10^{9} hz, J. Mol. Liquids, in press.

Furedi-Milhofer, H.; Babic-Ivancic, B.; Milat, O.; Brown, W. E.; Gregory T. M. Precipitation of sodium acid urate from electrolyte solutions. J. Crystal Growth 83: 572; 1987.

Brown, W. E.; Gregory, T. M.; Furedi-Milhofer, H. Computed phase diagrams for the system: sodium hydroxide, uric acid, hydrochloric acid-water. J. Crystal Growth 83: 588; 1987.

Babic-Ivancic, B.; Furedi-Milhofer, H.; Brown, W. E.; Gregory, T. M. Precipitation diagrams and solubility of uric acid dihydrate. J. Crystal Growth 83: 581; 1987.

Carey, C. M.; Tatevossian, A.; Vogel, G. L. The rapid deterioration of extracellular potassium concentrations in whole human dental plaque and plaque fluid. J. Dent. Res., in press.

Chang, S. S.; Pummer, W. J. Partitioning of vinyl chloride in poly(vinyl chloride) by head-space gas chromatography, ACS Polymer Preprints 28(1): 242; 1987.

Chang, S. S. Specific heat of hydrocarbon polymers, ACS Polymer Preprints 28(1): 244; 1987.

Chang, S. S. Heat of reaction and curing of epoxy resins. J. Thermal Anal., in press.

Chiang, C. K.; Bauer, B. J.; Briber, R. M.; Davis, G. T. Synthesis of ionic conducting interpenetrating polymer networks, Polymer Communications 28: 34; 1987.

Chiang, C. K.; Cook, L. P.; Chang, S. S.; Blendell, J.; Roth, R. S. Low temperature thermal processing of superconducting ceramics, Bull. Sp. Pub. Adv. Ceramics, in press.

Crissman, J. M.; Wang, F. W.; Guttman, C. M.; Maurey, J. R.; Wagner, H. L.; Fanconi, B. M.; VanderHart, D. L. Reference standard polyethylene resins and piping material, NBSIR 87-3506; 1987.

Crissman, J. M.; McKenna, G. B. A reduced variable approach to relating creep and creep rupture in PMMA. J. Poly. Sci. Poly. Phys. Ed., 25: 1667; 1987.

Davis, G. T. Piezoelectric polymer transducers. J. Dent. Res., in press.

Schoch, K. F.; DeReggi, A. S.; Roth, S. C. Apparatus for Quasihydrostatic Measurement of Piezoelectric d_h Coefficient, ISAF Proceedings, 1986.

DeReggi, A. S.; Broadhurst, M. G. Effects of space charge on the poling of ferroelectric polymers, Ferroelectrics 73: 351; 1987.

de Rijk, W. G.; Brown, W. E.; Chow, L. C. Clinical evaluation of a hydroxyapatite precipitate for the treatment of dentinal hypersensitivity in Bioengineering V, Current Concepts, S. Saha, ed., Pergamon Press, NY, 1986.

de Rijk, W. G.; Tesk, J. A.; Penn, R. W. The nonnormal distribution of failure stresses in a porcelain to metal systems evaluation. Proc. 6th Southern Bioengineering Conf., in press.

Dickens, B.; Martin, J. W.; Waksman, D. Analysis of damage profiles in poly(methyl methacrylate) in terms of oxygen diffusion and consumption. Polymers Degradation and Stability, Elsevier Applied Science Publishers, Barking, Essex, England, 15: 265; 1986.

Dickens, B.; Phillips, J. C. Studies of intaglio inks, NBSIR 87-3521; 1987.

Martin, J. W.; Dickens, B.; Waksman, D.; Bentz, D. P.; Byrd, W. E.; Embree, E.; Roberts, W. E. Thermal degradation of poly(methyl methacrylate) at 50C to 125C. J. Appl. Phys. Poly. Sci. 34: 377; 1987.

Di Marzio, E. A.; Guttman, C. M. The glass temperature of polymer rings. Macromolecules 20(6): 1403; 1987.

Di Marzio, E. A.; Passaglia, E. Calculations of the amount of adjacent re-entry in polymer crystallization, I. the basic equations, J. Chem. Phys. in press.

Eanes, E. D. Calcium phosphate formation in aqueous suspensions of anionic liposomes, Cell Mediated Calcification and Matrix Vesicles, Ali, S. Y., ed., Elsevier, Amsterdam, 1986, pp. 187-192.

Eanes, E. D.; Hailer, A. W. Calcium phosphate precipitation in aqueous suspensions of phosphatidylserine containing anionic liposomes. Calc. Tiss. Intl. 40: 43; 1987.

Eidelman, N.; Chow, L. C.; Brown, W. E. Calcium phosphate saturation levels in ultrafiltered serum, Calc. Tiss. Intl., 40: 71; 1987.

Eidelman, N.; Chow, L. C.; Brown, W. E. Calcium phosphate phase transformations in serum. Cal. Tiss. Intl. 41: 18; 1987.

Fanconi, B. M.; Wang, F. W.; Hunston, D. L. Comparisons among process monitoring techniques, Proc. Antec 87: 1100; 1987.

Fanconi, B. M.; Wang, F. W.; Lowry, R. E. Process monitoring of polymer matrix composites using fluorescence probes, Review of Progress in Quantitative Nondestructive Evaluation, 6B: 1287; 1987.

Arends, J.; Christoffersen, J.; Christoffersen, M. R.; Eckert, H.; Fowler, B. O.; Heughebaert, J. C.; Nancollas, G. H.;Yesinowski, J. P.; Zawacki, S. J. A calcium hydroxapatite precipitated from an aqueous solution - an international multimethod analysis. J. Crys. Growth, in press.

Mansfield, M.; Guttman, C. M.; Di Marzio, E. A. Models of chain folding in semicrystalline polymers. J. Poly. Sci. Poly. Lett. Ed. 24: 565; 1986.

Okada, M.; Han, C. C. Experimental study of thermal fluctuation in spinodal decomposition of a binary polymer mixture, J. Chem. Phys., 85(9): 5317; 1986.

Tran-Cong, Q; Chang, T.; Nishijima, Y.; Han, C. C. Application of a photodimerizable probe to the forced rayleigh scattering technique for measurement of self-diffusion of polymer chains. Polymer 27: 1705; 1986.

Han, C. C.; Tran-Cong, Q.; Chang, T. An intramolecular photodimerizable probe (bame) for mass diffusion measurements by the forced rayleigh scattering, Polymer Preprints, 28: 371; 1987.

Han, C. C.; Sato, T.; Okada, M.; Wu, C. Polymer diffusion in an interacting system, Polymer Preprints, 28: 358; 1987.

Hadziioannou, G.; Cotts, P.; ten Brinke, G.; Han, C. C.; Lutz, P.; Strazielle, C.; Rempp, P.; Kovacs, A. Thermodynamics and Hydrodynamic Properties of Dilute Solutions of Cyclic Polystyrenes, Macromolecules, 20: 493; 1987.

Hunston, D. L.; Moulton, R. J.; Johnston, N. J.; Bascom, W. D. Matrix resin effects in composite delamination: Mode-I Fracture Aspects. Toughened Composites, STP-937, ASTM 74; 1987.

Bascom, W.; Boll, D. J.; Hunston, D. L.; Fuller, B.; Phillips, P. J. Fractographic analysis of interlaminar fracture, Toughened Composites, STP 937, ASTM: 131; 1987.

Hunston, D. L.; Dehl, R. E. The role of polymer toughness in matrix dominated composite fracture, Autocom 87, SME, EM87-355; 1987.

Kinloch, A. J.; Hunston, D. L. The effect of volume fraction of dispersed rubber phase on the toughness of rubber-toughened epoxy polymers. J. Matl. Sci. Lett., 6: 137; 1987.

Bascom, W. D.; Hunston, D. L. The fracture of epoxy and elastomer-modified epoxy polymers. Treatise on Adhesion & Adhesives 6:, in press.

Heywood, B. R.; Eanes, E. D. An ultrastructural study of calcium phosphate formation in multilamellar liposome suspensions. Calc. Tiss. Intl. 41: 192; 1987.

Marqusee, J. A. One dimensional coagulation: scaling and phase separation dynamics, Phys. Rev. A 35: 1856; 1987.

Marqusee, J. A.; Mulholland, G. W. "Comment on: On the applicability of Smoluchowski's equation with a constant kernel to coalescence". J. Chem. Phys., in press.

Mathew, M.; Brown, W. E. A structural model for octacalcium phosphate-succinate double salt, Bull. Chem. Soc. Jpn. 60: 1141; 1987.

Mazur, J.; Reneker, D. H.; Fanconi, B. M. Longitudinal Acoustic Mode Frequencies of Polyethylene Chains Containing Defects, Polymer Communications 28: 78; 1987.

McKenna, G. B.; Guenet, J. M. The concentration of the compression modulus of isotactic polystyrene/cis-decalin gels, J. Poly. Sci., Part B: Phys. Ed. 24: 2499; 1986.

McKenna, G. B. Plazek, D. J. The viscosity of blends of linear and cyclic molecules of similar molecular mass, Poly. Comm., 27: 304; 1986.

McKenna, G. B.; Bullman, G. W.; Flynn, K. M.; Patt, J. Fatigue of a rubber tank track compound under tensile loading. Elastomers & Rubber Tech. ed. by R. E. Singler and C. A. Byrne, USGPO, Washington, DC, pp. 525, 1987.

McKenna, G. B.; Hadziiaonnou, G.; Hild, G.; Straziel1e, C.; Lutz, P.; Rempp, P.; Kovacs, A. J. The molecular weight dependence of the zero shear viscosity of cyclic polystyrene molecules in the melt. Macromolecules 20: 498; 1987.

McKenna, G. B.; Guenet, J. M. The effects of solvent type on the concentration dependence of the compression modulus of thermoreversible isotactic polystyrene gels. J. Poly. Sci., Poly. Phys. Ed., in press.

McKenna, G. B.; Rendell, R. W.; Ngai, K. L. The molecular weight and concentration dependence of the terminal relaxation time and viscosity of entangled polymer solution. Macromolecules, in press.

McKinney, J. E.; Antonucci, J. M.; Rupp, N. W. Wear and mirohardness of glass-ionomer cements. J. Dent. Res. 66(6): 1134; 1987.

Whitman, D. J.; McKinney, J. E.; Hinman, R. H.; Hesby, R. A.; Pelleu, G. M. In vitro wear rates of three types of commercial denture tooth materials. J. Prosth. Dent. 57(2): 243; 1987.

Misra, D. N. Adsorption of phenoxyacetic acid and trans-cinnamic acid on hydroxyapatite, Symp. on Surfactants in Solution, in press.

Misra, D. N.; Bowen, R. L.; Johnston, A. D. Adsorption of n-phenylglycine on hydroxyapatite, J. Dent. Res., in press.

Misra, D. N.; Bowen, R. L. Adsorption of PMDM, the adducts of pyromelletic dianhydride with 2-hydroxyethylmethacrylate, on hydroapatite, Special Edition Supplement to Journal of Colloid and Surfaces 26: 101; 1987.

Passaglia, E. The characterization of microenvironments and the degradation of archival records: a research program. NBSIR 87-3635, 1987.

Passaglia, E. Craze and fracture in polymers, J. Chem. Phys. Solids, in press.

Passaglia, E.; Di Marzio, E. A. Estimation of the amount of non-adjacent re-entry in polymer crystallization. II. application to once folded n-paraffins. J. Chem. Phys., in press.

Penn, R. W.; Craig, R.; Tesk, J. A. Diametral tensile strength and dental composites. Dent. Matl., 3: 46; 1987.

Bundy, K. J.; Penn, R. W. Improvement of metal/bone cement interfacial strength, J. Biomedical Matls. Res., in press.

Reneker, D. H.; Mazur, J. Small defects in crystalline polyethylene, Polymer, in press.

O'Sullivan, B.; Johnson, P.; Hesby, R.; Blosser, R.; Rupp, N. W.; Pelleu, G. Bonding strengths of a luting composite resin to dentin using different bonding systems, J. Pros. Dent., in press.

Hung, C.-C.; Shibata, J. H.; Tarpey, M. F.; Jones, A. A.; Porco, J. A.; Inglefield, P. T. Further studies of multiple nuclear spin relaxation and local motions in dissolved 1,1-dichloro-2,2-bis(4-hydroxyphenyl)-ethylene polyformal. Anal. Chimica Acta, 189: 167; 1986.

Roy, A. K.; Inglefield, P. T.; Shibata, J. H.; Jones, A. A. Local intermolecular structure in an antiplasticized glass by solid-state nmr. Macromolecules 20: 1434; 1987.

Smith, L. E.; Verdier, P. H. Polymer standards, Enc. of Poly. Sci. & Eng., 12, in press.

Takagi, S.; Mathew, M.; Brown, W. E. The crystal structures of natural bobierrite and synthetic $Mg_3(PO_4)_2.8H_2O$, American Mineralogist 71: 1229; 1986.

Takagi, S.; Chow, L. C.; Yamada, E. M.; Brown, W. E. Enhanced enamel f uptake by monocalcium phosphate monohydrate gels. J. Dent. Res., in press.

Kuriyama, M.; Dobbyn, R.C.; Takagi, S.; Chow, L. C. Microradiography with an x-ray image magnifier: application to dental hard tissue. Med. Phys., in press.

Dobbyn, R. C.; Kuriyama, M.; Takagi, S.; Chow, L. C. High resolution radiography: application to biomedical imaging, Proc. 6th Southern Biomedical Enginering Conference, in press.

Tesk, J. A. Research opportunities for American industry at NBS, ADTA Newsletter, January-April, 1987.

Tesk, J. A. Dental materials research at the National Bureau of Standards, opportunities for industry, Trends and Techniques 4(6): 5; 1987.

Tesk, J. A.; Antonucci, J. A.; Brauer, G. M.; McKinney, J. E.; Penn, R. W.; Stansbury, J. W.; de Rijk, W.; Venz, S.; Iizuka, H.; Lee, S.; Asaoka, K. Properties and interactions of oral structures and restorative materials, NBSIR 87-3539, 1987.

Tesk, J. A. High temperature dental investments, Book Chapter, in press.

Engler, R. A.; deRijk, W. G.; Tesk, J. A. and Morris, D. Multi-dimensional internal setting expansion of a phosphate-bonded casting investment measured with strain gauges. J. Prosthetic Dent., in press.

Hirano, S.; Tesk, J. A. Hinman, R.; Argentar, H.; Gregory, T. Casting of dental alloys mold and alloy temperature effects, Dent. Matl., in press.

Tesk, J. A. Review of the paper: casting metals by Kamal Asgar, J. Dent. Res., in press.

Tomazic, B.; Etz, E-; Brown, W. Nature and properties of cardiovascular deposites, Scanning Microscope 1: 95; 1987.

Tomazic, B. B.; Brown, W.E.; Queral, L. A.; Sadovnik, M. Physicochemical characterization of cardiovascular calcified deposits. I. isolation, purification and instrumental analysis. Atherosclerosis, in press.

VanderHart, D. L. Natural abundance ^{13}C--^{13}C spin exchange in rigid crystalline organic solids, J. Mag. Res. 72: 13; 1987.

VanderHart, D. L.; Atalla, R. H. Further ^{13}C NMR evidence for the coexistence of two crystalline forms of native celluloses. ACS Symp. Series 340: 88; 1987.

VanderHart, D. L.; Manders, W. F.; Stein, R. S.; Herman, W. A proton MAS NMR method for determining intimate mixing in polymer blends. Macromolecules 20: 1724; 1987.

VanderHart, D. L.; Perez, E. Morphological partitioning of chain ends and methyl branches in melt crystallized polyethylene by ^{13}C NMR. J. Poly. Sci. Poly. Phys. Ed. 25: 1637; 1987.

Perez, E.; VanderHart, D. L.; Crist, B.; Howard, P. R. Morphological partitioning of ethyl branches in polyethylene by ^{13}C NMR. Macromolecules 20: 78; 1987.

Perez, E.; VanderHart, D. L. Solid state ^{13}C NMR investigation of polyoxetanes. Polymer 28: 733; 1987.

Resing, H. A.; VanderHart, D. L.; Coronene as a model of charcoal: calibration of the carbon-13 NMR shift tensor to count carbon atoms at the plane edge. Zeit. f. Phys. Chem. 151: 137; 1987.

Verdier, P. H.; Kranbuehl, D. E. Simulation of polymer chain dynamics by lattice models with excluded volume:lattice dependence. Macromolecules 20(6): 1362; 1987.

Vogel, G. L.; Carey, C. M.; Chow, L. C.; Gregory, T. M.; Brown, W. E. Ultramicro analysis of the fluid in human enamel during in vitro caries attack by hydrochloric acid. Caries Res. 21: 310; 1987.

Wagner, H. L. The Mark-Houwink-Sakurada relation for poly(methyl methacrylate), J. Phys. Chem. Ref. Data 16: 165; 1987.

Wang, F. W.; Lowry, R. E.; Fanconi, B. M. Novel fluorescence method for cure monitoring of epoxy resins. Polymer 27: 1529; 1986.

Wang, F. W.; Fanconi, B. M. In-situ characterization of the interface of glass reinforced composites, NBSIR 87-3581, 1987.

Wang, F. W.; Wu, E. S. Cure monitoring of epoxy resins by fluorescence recovery after photobleaching, Polymer Communications 28: 73; 1987.

Kuentzler, R.; and Waterstrat, R. M. Electronic, magnetic, superconducting and amorphous-forming properties versus stabiity of the Ti-Fe, Zr-Ru and Hf-Os ordered alloys. J. Less-Common Metals 125: 261; 1986.

Wu, W. L. Molecular mechanism of deformation in epoxies, Proc. of Materials Research Society, December 1986.

Wu, W. L.; Gilmer, J. W. Molecular weight measured by scattering techniques in random block copolymers. Poly. Comm. 28: 202; 1987.

Wu, W. L.; McKinney, J. E. Glass transition temperature in dental composite resins. J. Dent. Res., in press.

Technical and Professional Committees: Leadership Activities

Academy for Dental Materials
J. A. Tesk, J. Dental Materials, Reviewer, 1987

Academy of Operative Dentistry
N. W. Rupp, Past President

Alpha Chi Sigma
G. M. Brauer, Member, Awards Committee
C. M. Carey, President, American University Chapter

American Academy of Gold Foil Operators
N. W. Rupp, President

American Academy of Implant Dentistry
J. A. Tesk, J. Oral Implantology, Academic Referee

American Association for Dental Research/International Association for Dental Research
L. C. Chow
Member, Fellowship Committee

E. A. Eanes
Member, Science Awards Committee
Chairman, Biological Minerlization Award Subcommittee
Councilor, Mineralized Tissue Group-AADR

J. A. Tesk
J. Dental Research Reviewer, 1987

American Association of Dental Research - Washington Section
J. M. Antonucci, Secretary-Treasurer

L. C. Chow, Vice President

American Chemical Society
G. M. Brauer
Alternate Councilor

C. C. Han
Co-Chairman for the Symposium on Polymer Diffusion, 1987

American Dental Association
R. L. Bowen
Member, Biomedical Research Support Grant Committee

American National Standards Committee, MD 156, Dental Materials, Instruments, and Equipment
R. L. Bowen
Secretary, Subcommittee on Biological Evaluation of Dental Materials

Member, Subcommittee on Direct Filling Resins

G. M. Brauer
Chairman, Subcommittee on Denture Resins
Member, Dental Materials, Instruments and Equipment
Member, Zinc Oxide-eugenol and Modified ZOE Cements Subcommittee

N. W. Rupp
Chairman, Group I Restorative Materials
Member, Subcommittee #1 - Alloy for Dental Amalgams
#6 - Mercury for Dental Amalgams
#29 - Fissure Sealants
#43 - Dispersers for Alloy & Mercury
#55 - Electrically Powered Amalgamators

J. A. Tesk
Chairman, Dental Materials, Instruments and Equipment
Member, Dental Implants Subcommittee
Chairman, USA TAG for ISO TC 106
Member, Porcelain Alloys Subcommittee
Member, Surgical Gloves Subcommittee

American National Standards Institute (ANSI)

W. de Rijk
Member, Subcommittee Gypsum Products & Investments
Waxes (Spec #4 and 24)

J. A. Tesk
Member, Medical Devices Standards Management Board

American Physical Society
G. B. McKenna
Division of High Polymer Physics
Member, Publications Committee

M. G. Broadhurst
Member, Executive Committee

American Society for Metals
R. M. Waterstrat
Member, Alloy Phase Diagram Data Committee

American Society for Testing and Materials (ASTM)
G. M. Brauer
Member, Executive Committee, F-4 Medical and Surgical Materials, and Devices
Chairman, Polymeric Materials Section
Member various task forces
Member, TAG/TC 150

S. S. Chang
Member, D37 Thermal Measurements
    D37.01 Test Methods
    D37.05 Thermophysical Properties

C. M. Guttman
Member, D20.30 Thermal Properties
    D20.70 Analytical Methods
E-37 - Subcommittee on Thermal Analysis
Chairman, Task Group on Purity Standards and Methods

D. L. Hunston
Member, D30 High Modulus Fibers & their Composites

G. B. McKenna
Member, D-11 Rubber and Rubber-like Materials
Member, E-9 Fatigue

L. J. Zapas
D-2 Petroleum Products and Lubricants
Member: D2.07 Flow Properties
    D2.07A Newtonian Viscometry

Case Western Reserve University
Dental School, Long-Range Planning Committee
Member, J. A. Tesk

Chemical Society of Washington
J. M. Antonucci
Member, Board of Managers

G. M. Brauer
Chairman, Awards Committee
Member, Public Relations Committee
Member, Long Range Planning Committee

DoC Small Business Innovation Research Program
M. G. Broadhurst
Contracting Officers Technical Representative

Experimental NMR Conference
D. L. VanderHart
Member, Executive Board

Engineering Foundation Conference: Dentistry
J. A. Tesk, Chairman 1987

Gordon Conference: Calcium Phosphates
L. C. Chow
Co-chairperson, 1989

Gordon Conference: Thermosetting Polymers
D. L. Hunston
Chairman 1987

Institute of Electrical & Electronic Engineers (IEEE)
Conference on Electrical Insulation & Dielectric Phenomena
A. S. DeReggi
Member, Board of Directors

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

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

International Standards Organization
TC106, Dental Materials and Devices

N. W. Rupp
Member, Restorative Materials
Chairman, SC.01, U.S. Delegation
Chairman, ATG7, Alloys for Dental Amalgams
SC6 WG5 Electrically Powered Amalgamators

Macromolecules
E. A. Di Marzio
Member, Editorial Review Board

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

National Bureau of Standards Committee on University of Maryland
Instructional Television System
E. A. Di Marzio, Member

National Bureau of Standards Editorial Review Board
E. A. Di Marzio, Member

National Bureau of Standards Research Advisory Panel
E. A. Di Marzio, Member

National Center for Small Angle Scattering
C. C. Han
Member, Users Committee

National Institute Dental Research
J. M. Antonucci
Special Review Committee for Research Centers of
Oral Biology ADHOC Review

Special Study Sections for Small Business Innovative Research (SBIR) Grant Applications, Reviewer for SBIR Site Visit

National Science Foundation Advisory Board
 Regional NMR Facility at Colorado State University
 D. L. VanderHart

Office of Naval Research
 J. M. Antonucci
 Bioengineering for Materials Application (BEMA) Research Program Review Meeting, 1987

 Member of the Molecular Biology Program/Office of Naval Research Oversight Panel

Office of Science and Technology Policy
 D. H. Reneker
 Executive Secretary, Committee on Materials (COMAT)

Plastics Institute of America
 D. H. Reneker

Polymers Division Editorial Committee
 P. H. Verdier, Chairman

Polymers Gordon Conference (West)
 E. A. Di Marzio, Vice-Chairman & Chairman Elect, 1988-89

Society of Rheology
 G. B. McKenna
 Member, Committee on Education

 D. L. Hunston
 Member, Committee on Education
 Member, Site Selection Committee

U. S. Air Force
 N. W. Rupp
 Surgeon General's Civilian Consultant on Dental Materials

U. S. Navy Research
 Department of Naval Dental School
 J. A. Tesk, Consultant

U.S. Yugoslav Joint Scientific and Technological Cooperative Program
 W. E. Brown
 NBS Member

VAMAS
C. C. Han
Member, Technical Working Party on Polymer Blends

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

Visiting Committee for Lehigh University
D. H. Reneker
Member, Department of Metallurgy & Materials Engineering

Industrial and Academic Interactions

Industrial

A Research Associate agreement has been established with AT&T Bell Laboratories to develop a fluorescence technique for monitoring the formation of polyimide polymers. The objective is to measure, in-situ and on-line, the changes in fluorescence spectra occurring during the formation of polyimide polymers from poly(amide-acid) precursors.

A Research Associate agreement has been established with the Mead-Hope Battery Joint Venture group to transfer NBS solid polymer electrolyte technology. The group is particularly interested in the poly(ethylene oxide)/epoxy interpenetrating network developed and patented by NBS, and will be preparing a series of these new materials at NBS for further evaluation of their potential commercial usefulness.

A four year research program with Hercules, Hexcel, and NASA Langley Research Center on delamination in composite materials was completed this year. Hercules and Hexcel provided materials and some fracture surface analysis, NASA characterized the samples, and NBS determined interlaminar fracture behavior. The results, reported in two publications, define the effect of resin toughness on interlaminar fracture, and provide an important guideline to industry in their efforts to develop more damage tolerant composites.

Research Associate agreements form the basis of ongoing work to transfer to Westinghouse techniques to measure compliant piezoelectric materials, to transfer to IMASS Corporation technology for commercialization of the time domain dielectric spectrometer, and to transfer to General Electric Corporation the technology for duplication of the spectrometer for use in their corporate laboratories.

A joint program is being developed with Dexter-Hysol on structure-property relationships in composites. Three potential areas of focus are the fiber matrix interface, the structure of fibers, and toughening of the resin. Dexter-Hysol will provide specially prepared samples and NBS will use small angle neutron scattering to characterize the materials.

Standard reference materials have been issued for polyethylene resins of the sort used in natural gas distribution systems. Production of the SRM was supported by the Gas Research Institute which is also funding studies of the effects of processing polyethylene resins into pipes and fittings. The reference materials will facilitate test method development, standardization of test methods, and inter-laboratory comparisons of test data.

A Research Associate agreement with SICPA, Virginia, will transfer piezoelectric and pyroelectric polymer technology for possible addition of commercial polymer sensors to their product line.

A three year joint project with the University of Connecticut has been completed. The work, funded by the Electric Power Research Institute, related the effects of space charge to breakdown in polymer insulated DC power cables. Thermal pulse measurements at NBS and thermally stimulated current measurements at U. Conn. supplemented each other.

The effects of processing on the molecular network structure of epoxy resins is being investigated with the help of a scientist from Texaco. Texaco is providing the raw materials, using gel permeation chromatography, to measure molecular weight distributions and conducting mechanical tests to determine toughness of the cured resins. NBS is correlating these results with molecular structure information obtained by small angle neutron scattering and establishing processing-structure-property relationships.

Molecular composites are being characterized for the degree of dispersion of the rigid rod polymers in thermoplastic matrix resins. The specimens are supplied by Dow and duPont which are developing methods of processing these experimental materials to achieve uniform dispersion of the rigid rod polymers. It is postulated that maximum mechanical properties are achieved with good dispersion.

Joint blends-related projects are underway with several large companies. Specific polymer compositions of interest to Exxon, IBM, Eastman Kodak, and Shell Development Company will be emphasized, and the work will focus on phase stabilization problems of interest to IBM and Eastman Kodak, and on barrier properties and processing of materials from Armstrong World Incorporated.

The American dental industries continue to display strong support for the dental materials program. The research associate agreement with Dentsply International was extended to its fourth year and a new research associate from Astron Dental Corporation is helping develop improved polymeric prosthetic materials. A new research associate agreement with Genex Corporation is for adhesion testing of bioadhesives genetically developed from protein, and an agreement with Pentron Corporation is being explored.

Industrial/Academic

A joint NBS-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 tire industry.

Academic

The failure behavior of toughened polymers is the subject of cooperative work with Dr. A. J. Kinloch at Imperial College. Scientists at NBS are determining fracture behavior while those at Imperial College are characterizing the morphology of the same multiphase polymer systems. The ultimate objective is the development of structure-property relationships for such materials.

The University of Pennsylvania is cooperating with NBS scientists to study the scattering behavior of condensation polymers during interchain exchange reactions.

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.

A joint program is underway with the Charles Sadron Institute, Strasbourg, France to characterize the structure and mechanical properties of polystyrene gels. The validity of models that postulate ordered solvent and different molecular structure for polystyrene in the gel state are being tested.

A joint research program with the University of Maryland produced a manuscript on cure monitoring of epoxy resins by fluorescence recovery after photobleaching. An instrument to determine diffusion in polymer systems by measuring fluorescence recovery after photobleaching was built as part of the program.

In cooperation with William and Mary College, a manuscript on simulation of polymer chain dynamics by lattice models with excluded volume was published.

Guest scientists from three domestic and two foreign universities are conducting research on dental materials at NBS. A cooperative seminar series with the University of Maryland Dental School is in progress. Several finite element modelling studies on dental material-tooth systems continue with the University of Illinois, Chicago. The use of Weibull statistics for characterization of failure of dental materials is being pursued with the Washington State University. Tokushima University is collaborating on two dimensional finite-element analyses of build-up of stress in quenched dental materials and Tokyo University on dental castings.

A joint research program with the Universite de Nantes, France and the Universita di Milano, Italy has led to determination of effective conjugation lengths in polyacetylene samples of differing molecular weights using Resonance Raman Scattering. A manuscript on this subject was submitted for publication.

Associated Activities

Invited Talks

Division personnel presented a total of 86 invited talks on research activities at the following types of organizations and symposia: industrial laboratories, 12; international symposia, 7; universities, 23; topical symposia, 0; national and government laboratories, 14; professional society meetings, 27; and Gordon Conferences, 3.

SRMS

The certificates for two poly(methyl methacrylate) SRM's (1488 and 1489) have been issued. These SRM's will be used by the polymers industry to calibrate instruments used to measure the molecular weight and molecular weight distributions of acrylic type polymers.

The certificate for SRM 1497, a pigmented polyethylene gas pipe resin, is being issued. This SRM will be useful not only to the gas distribution and associated industries but also to the scientific community.

Patents

Antonucci, J. M. Hydrophobic Dental Composites Based on a Polyfluorinated Dental Resin, U. S. Patent No. 4,616,073, October 7, 1986.

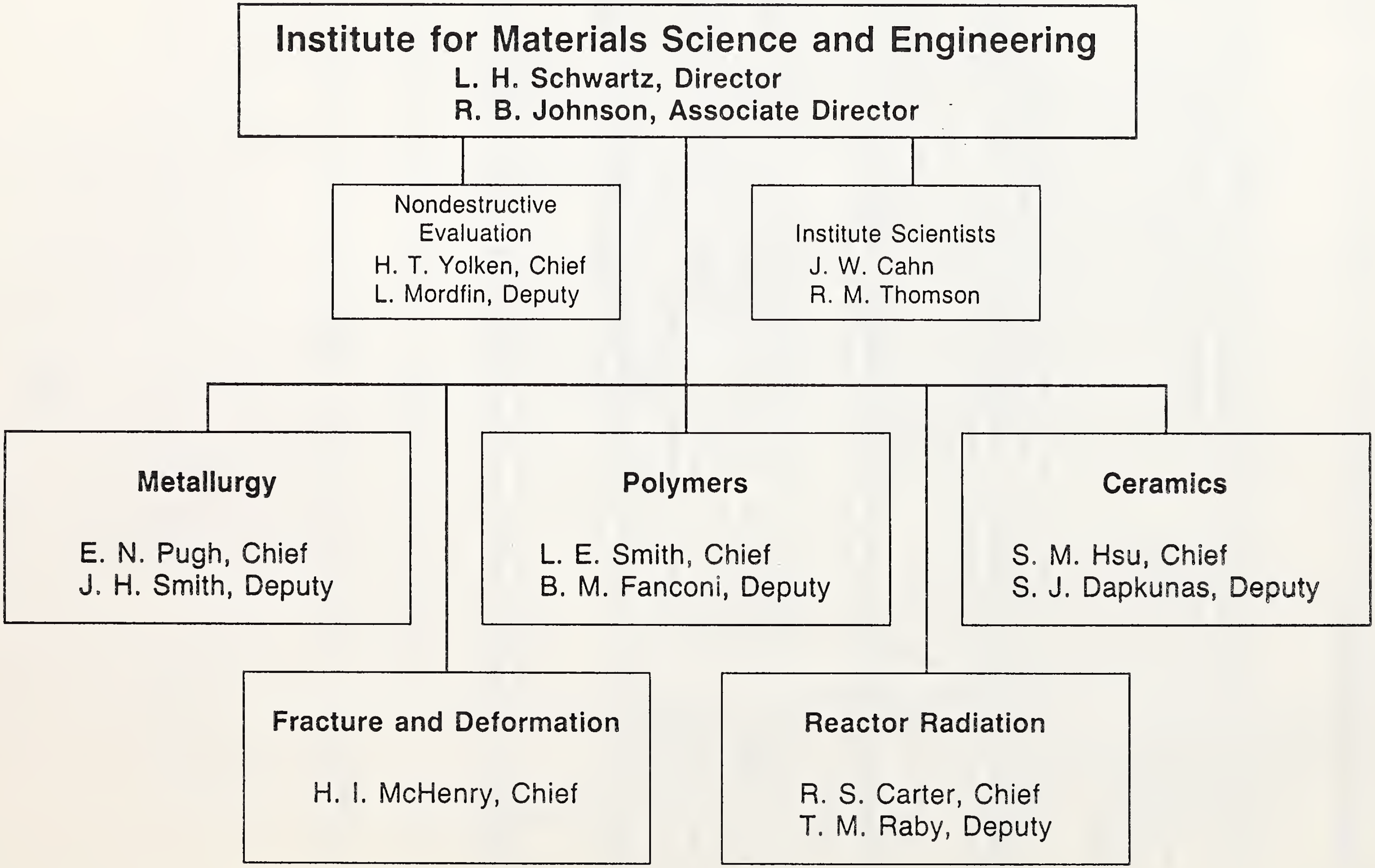
Bauer, B. J.; Chiang, C. K.; Davis, G. T. Interpenetrating-Network Polymeric Electrolytes, U. S. Patent No. 4,654,279, March 31, 1987.

Bowen, R. L. Method for Obtaining Strong Adhesive Bonding of Composites to Dentin, Enamel and Other Substrates, United Kingdom Patent No. 2159067, March 4, 1987.

Bowen, R. L. Simplified Method for Obtaining Strong Adhesive Bonding of Composites to Dentin, Enamel and Other Substrates, U. S. Patent No. 4,659,751, April 21, 1987.

Harris, G. R.; De Reggi, A. S. Transducer Hydrophone with Filled Reservoir, U. S. Patent No. 4,653,036, March 24, 1987.

Waterstrat, R. M. Arc-furnace for the Production of Small Investment Castings, U. S. Patent No. 4,627,482, December 9, 1986.



Institute for Materials Science and Engineering
L. H. Schwartz, Director
R. B. Johnson, Associate Director

Nondestructive Evaluation
H. T. Yolken, Chief
L. Mordfin, Deputy

Institute Scientists
J. W. Cahn
R. M. Thomson

Metallurgy
E. N. Pugh, Chief
J. H. Smith, Deputy

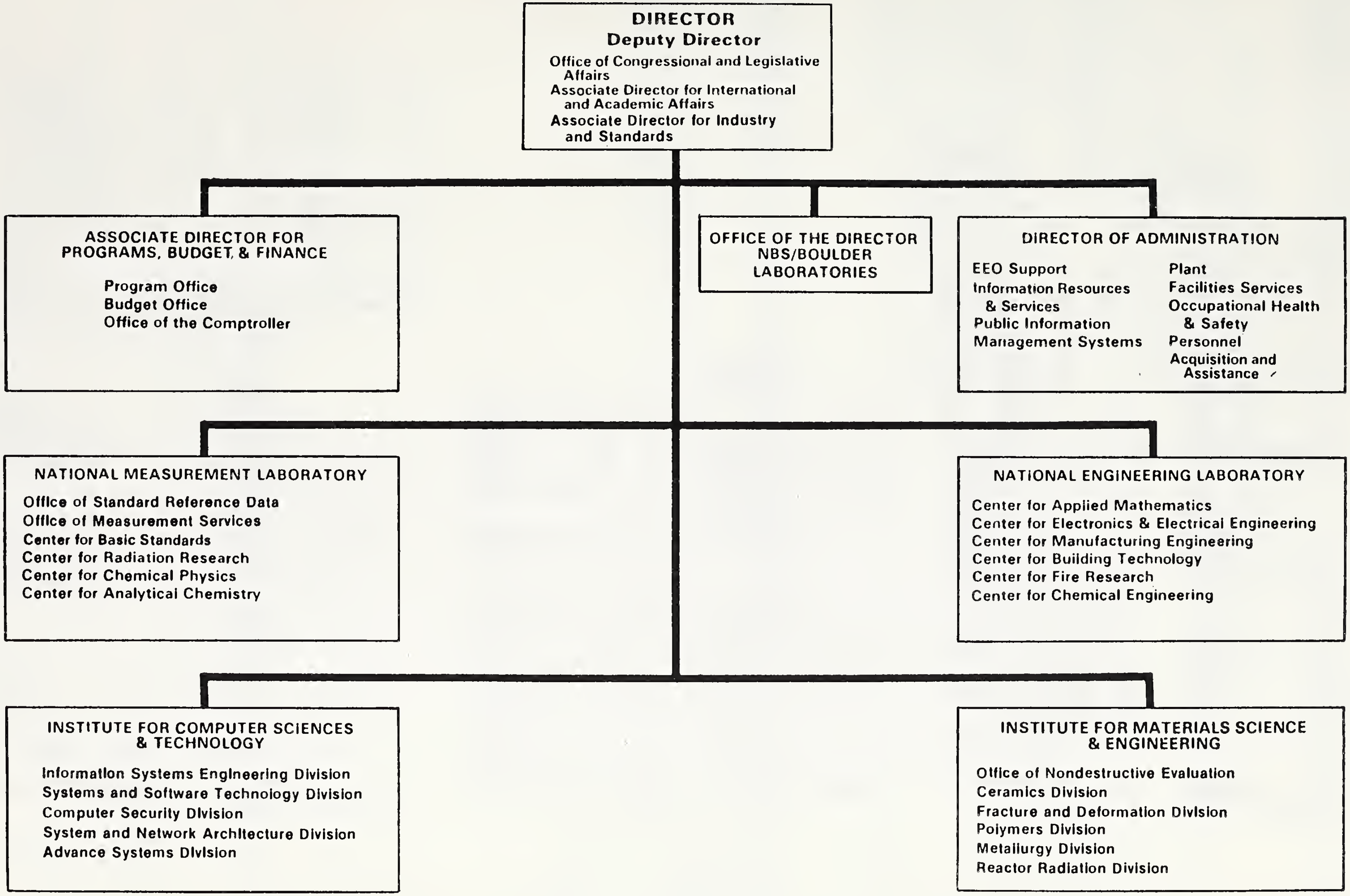
Polymers
L. E. Smith, Chief
B. M. Fanconi, Deputy

Ceramics
S. M. Hsu, Chief
S. J. Dapkunas, Deputy

Fracture and Deformation
H. I. McHenry, Chief

Reactor Radiation
R. S. Carter, Chief
T. M. Raby, Deputy

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards



DIRECTOR
Deputy Director

Office of Congressional and Legislative Affairs
Associate Director for International and Academic Affairs
Associate Director for Industry and Standards

ASSOCIATE DIRECTOR FOR PROGRAMS, BUDGET, & FINANCE

Program Office
Budget Office
Office of the Comptroller

OFFICE OF THE DIRECTOR NBS/BOULDER LABORATORIES

DIRECTOR OF ADMINISTRATION

EEO Support
Information Resources & Services
Public Information
Management Systems
Plant
Facilities Services
Occupational Health & Safety
Personnel
Acquisition and Assistance

NATIONAL MEASUREMENT LABORATORY

Office of Standard Reference Data
Office of Measurement Services
Center for Basic Standards
Center for Radiation Research
Center for Chemical Physics
Center for Analytical Chemistry

NATIONAL ENGINEERING LABORATORY

Center for Applied Mathematics
Center for Electronics & Electrical Engineering
Center for Manufacturing Engineering
Center for Building Technology
Center for Fire Research
Center for Chemical Engineering

INSTITUTE FOR COMPUTER SCIENCES & TECHNOLOGY

Information Systems Engineering Division
Systems and Software Technology Division
Computer Security Division
System and Network Architecture Division
Advance Systems Division

INSTITUTE FOR MATERIALS SCIENCE & ENGINEERING

Office of Nondestructive Evaluation
Ceramics Division
Fracture and Deformation Division
Polymers Division
Metallurgy Division
Reactor Radiation Division

SMITH, LESLIE E., DR., CHIEF

FANCONI, B. M., DR., DEP. CHIEF

BROADHURST, M. G., DR., ASST. CHIEF

THOMAS, S. M., ADMIN. OFFICER
HYDE, B. A., SECRETARY

Consultant
CLARK, E. S., Dr.

ELECTRICAL PROPERTIES

DAVIS, G. T., DR.
HOFFMASTER, L. A.

DEREGGI, A. S., DR.
KRYDER, S. J.
MOPSIK, F. I., DR.
ROTH, S. C.
SCHEN, M. A., DR.

Research Associates
CHEN, D., DR.
DEROSSI, D., DR.
FRANK, E. H., DR.
HANSEN, C., DR.
SCHOCH, K. F., DR.

Guest Scientists
BARKER, R. E., DR.
EBY, R. K., DR.
EDELMAN, S.
HARRIS, G. R., DR.

CHEMICAL PERFORMANCE & STANDARDS

WANG, F. W., DR.
HOFFMASTER, L. A.

BUR, A. J., DR.
DEHL, R. E., DR.
GUTTMAN, C. M., DR.
LOWRY, R. E.
MAUREY, J. R.
VERDIER, P. H., DR.

Guest Scientists
DILLON, J. G., DR.
FLORIN, R. E., DR.
FLYNN, J. H., DR.
GRANT, W. H., Dr.
KRANBUEHL, D. E., DR.
WAGNER, H. L., DR.
WILSON, W. K.

Students
CLARK, S.

MECHANICAL PERFORMANCE

FANCONI, B. M., DR.
CHAPWICK, N. C.

CRISSMAN, J. M., DR.
FLYNN, K. M.
KHOURY, F. A., DR.
MCKENNA, G. B., DR.
RENEKER, D. H., DR.
VANDERHART, D. L., DR.
ZAPAS, L. J., DR.

Research Associates
KEARSLEY, E. A., DR.

Guest Scientists
BRENNA, A.
HOWELL, B. F., DR.
MANDERS, W. F., DR.
MAZUR, J., DR.
PETERLIN, A., DR.
WOOD, L. A., DR.

POLYMER COMPOSITES

HUNSTON, D. L., DR.
RUFF, J. E.

BAUER, B. J., DR.
BULLMAN, G. W.
CHANG, S. S., DR.
DICKENS, B., DR.
LEE, A., DR.
PASSAGLIA, E., DR.
WU, W. L., DR.

Guest Scientists
BRINGUIER, A. G.
GILMER, J. W.
HINKLEY, J. A., DR.
KOBERSTEIN, J. T., DR.
LICHKUS, A. M.
SMITH, J. C., DR.
STIEHLER, R. D., DR.

Students
FOSSETT, J. T.
PRAHINSKI, J.

POLYMER BLENDS

HAN, C. C., DR.
BURTON, J. S.

BARNES, J. D., DR.
BRIBER, R. M., DR.
CLARK, J. C., DR.
DI MARZIO, E. A., DR.

Research Associates
COLBY, R. H., DR.
HADZIIOUNNOU, G., DR.
LANDRY, M., DR.
LOHSE, D., DR.
MASON, M. G., DR.
MASSA, D. J., DR.
O'REILLY, J. M., DR.
RUSSELL, T. P., DR.
WELCH, W. C., DR.
YANG, H. E., DR.

Guest Scientists
AMIS, E. J., DR.
BERARD, M.T., DR.
LODGE, T. P., DR.
MARQUSEE, J. A., DR.
MCCRACKIN, F. L., DR.
MORRISON, F. A., DR.
NOJIMA, S., DR.
ROE, R. J., DR.
SONI, V. K., DR.
SUNG, P., DR.

Students
MURPHY, D. G.

DENTAL & MEDICAL MATERIALS

TESK, J. A., DR.
HARLOW, S. F.

ANTONUCCI, J. M., DR.
BRAUER, G. M., DR.
DE RIJK, W., DR.
MCKINNEY, J. E.
STANSBURY, J. W., DR.

Research Associates
EANES, E. A., DR.
FOWLER, B. O.
HAILER, A. W.
MULLER, R., DR.
VENZ, S., DR.

Guest Scientists
BUSHNESS, G. F., DR.
CHOHAYED, A.
COBB, E., DR.
FORSYTHE, L. L., DR.
FUKASE, Y., DR.
HEYWOOD, B. R.
LEE, C., DR.
MARKOVIC, M., DR.
MEYER, J., DR.
PALMER, D. S., DR.
PENN, R. W., DR.
SUGAWARA, A., DR.
THOMPSON, V. P., DR.

Students
JOHNSON, K.
MARSH, J.

Dental and Medical Materials Group

American Dental Association Research Associates
BOWEN, R. L., DR., DIRECTOR
BLOSSER, R. L.
BROWN, W. E., DR.
CAREY, C. M.
CHALKLEY, M. W.
CHOW, L. C., DR.
CONNER, M. L.
EICHMILLER, F., DR.
EIDELMAN, N., DR.
GIUSEPPETTI, A. A.
GREGORY, T. M.
JOHNSTON, A. D., DR.
KIRKPATRICK, D., DR.
LY, A. K., DR.
MARJENHOFF, W.A.
MATHEW, M., DR.
MISRA, D. N., DR.
PRESTEMON, E. F.
RUPP, N. W., DR.
SCHREIBER, C. T.
SIECK, B.
TAKAGI, S., DR.
TOMAZIC, B. B., DR.
TUNG, M. S., DR.
VOGEL, G. L., DR.
WATERSTRAT, R. M., DR.

NBS-114A (REV. 2-8C)

U.S. DEPT. OF COMM. **BIBLIOGRAPHIC DATA SHEET** *(See instructions)*	1. PUBLICATION OR REPORT NO. NBSIR 87-3614	2. Performing Organ. Report No.	3. Publication Date November 1987

4. TITLE AND SUBTITLE

Polymers Division: Technical Activities 1987

5. AUTHOR(S)

L. E. Smith and B. M. Fanconi

6. PERFORMING ORGANIZATION *(If joint or other than NBS, see instructions)*

NATIONAL BUREAU OF STANDARDS
DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20234

7. Contract/Grant No.

8. Type of Report & Period Covered
Annual Report
10/1/86 - 9/30/87

9. SPONSORING ORGANIZATION NAME AND COMPLETE ADDRESS *(Street, City, State, ZIP)*

National Bureau of Standards
Institute for Materials Science & Engineering
Polymers Division, Gaithersburg, MD 20899

10. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)*

Technical Activities of the Polymers Division for FY 87 are reviewed. Included are descriptions of the 6 Tasks of the Division, project reports, publications, and other technical activities.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

National Bureau of Standards; Polymers Division; Review; Technical Activities

13. AVAILABILITY

☒ Unlimited
☐ For Official Distribution. Do Not Release to NTIS
☐ Order From Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.
☒ Order From National Technical Information Service (NTIS), Springfield, VA. 22161

14. NO. OF PRINTED PAGES
103

15. Price