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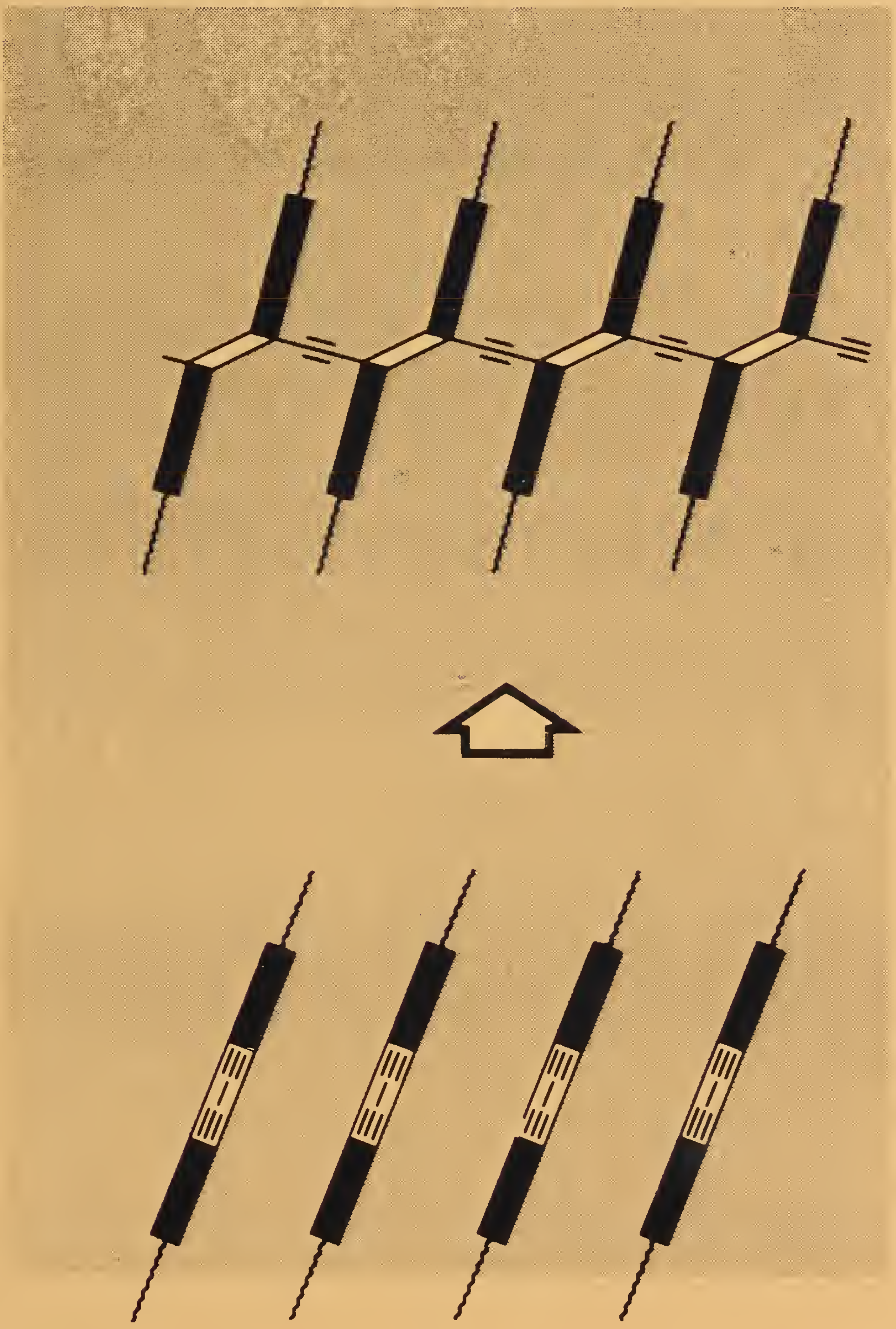
Institute for Materials Science and Engineering

POLYMERS



NAS-NRC
Assessment Panel
November 16-17, 1988

NISTIR 88-3842
U.S. Department of Commerce
National Institute of Standards
and Technology

Technical Activities 1988

Idealized representation of the molecular packing of a novel liquid crystalline diacetylene monomer and resulting polymer. The reactive diacetylene unit composed of alternating triple-single-triple bonds forms the core of the rigid mesogenic unit, represented by the blackened rectangle, of the liquid crystalline monomer. Polymerization within the various smectic and nematic liquid crystal phases gives rise to an organized pi-conjugated polymer structure composed of an alternating single-triple-single-double bond backbone repeat unit. Polydiacetylenes are of strong theoretical and technological interest in the expanding field of nonlinear optical polymers and integrated optics.

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

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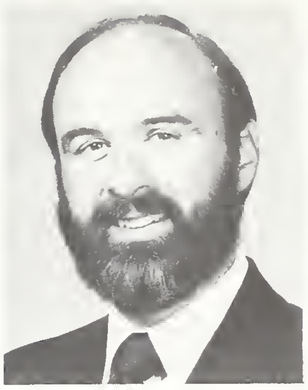

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BRUNO M. FANCONI, Group Leader, Mechanical Performance.

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INTRODUCTION

POLYMERS DIVISION

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

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

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

Based on the opinions of the participants in an industry workshop held at NIST in October, 1987, we have planned a program to study the behavior of polymers in transfer molding processes. Such processes inject a thermoplastic melt or a reacting thermoset mixture into a mold containing a fiber preform. Current work on sensors described in this report will be joined during the coming year by a modeling program which will describe the flow of polymer fluids under process conditions.

A second barrier to the more widespread use of polymer composites is our limited ability to measure and understand the way these materials perform or fail in service. The highly anisotropic properties that allow composites to be tailored for a specific application make their failure behavior very complex. Composite properties are also highly dependent on their processing conditions. This means that a meaningful composites program must integrate the mechanics of composites with an understanding of the materials science of the polymer matrix, the fibers, and the influence of process conditions. This is the goal of the next phase of our program which we hope to expand in 1990.

Biodegradation has become a household word as many parts of the country try to find solutions to the problem of municipal solid waste. Many states and localities have begun to define materials in laws in advance of our technical capability to measure or even agree on the meaning of terms. Recent federal laws will require certain materials to be degradable under some conditions and we see a need for standards and test methods in these areas. Several scientists with experience in microbiology and in the analysis of degradation products joined the Division this year. They will be exploring the technical issues involved in measuring biodegradation and particularly trying to produce reference materials that can standardize such measurements.

Technology transfer to industry continues to be a major concern of all of the Division's programs. The most effective method is through direct interaction with individuals from industry who know both their business and technical needs. Many of these interactions come through scientists who collaborate with us on technical projects. Last year the Division cooperated with 52 Research Associates and 82 Guest Scientists who together spent 50 staff years of effort at our laboratories. In addition, many industrial scientists have spent one or two days using specialized equipment developed by Division scientists to explore future research collaboration or to make proprietary measurements on their developmental materials.

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

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 along with references to the pages of the report where more information about the work may be found.

- In the design of polymers for nonlinear optics, diacetylene monomers which undergo multiple transitions to liquid crystalline states prior to melting have been synthesized. Thermally activated polymerization has been shown to occur not only in the solid state but also within the liquid crystalline states, with an activation energy of only 40% of that in the solid state. Furthermore, the resulting orange-colored polymer retains much of the long-range order present in the liquid-crystal precursor. (page 8)

- Certification measurements have been completed for a poly(methyl methacrylate) Standard Reference Material, SRM 1487. Produced with partial support from the Navy, this SRM will be used for quality control of antifouling paints and as a calibrating material for the analysis of acrylic polymers. Material has also been obtained and work started on the first of two polyurethane Standard Reference Materials, produced with partial support from the Food and Drug Administration, which will help meet a growing need for better methods of characterizing polyurethanes used in medical devices. (page 13, 14)

- A sensor has been designed to measure velocity, velocity gradients, and flow instabilities. The sensor operation is based on fluorescence recovery after photobleaching. A mathematical model to describe its behavior has been formulated. (page 15)

- Significant removal of phosphorus from an industrial iron ore concentrate by metabolic products of microorganisms was shown. This treatment offers a potential method for upgrading domestic iron ores that contain elevated levels of phosphorus to provide higher quality raw material for steel making. (page 19)

- An off-resonance NMR method was developed which is most useful to resolve methylene and methine resonances in rigid solids. Separation of methine and methylene resonances is important in cases where the chemical structures are not completely known or where resonance assignments are required. (page 25)

- A constitutive equation has been developed which, for the first time, describes the nonlinear mechanical response in a stress relaxation experiment for a semi-crystalline polymer. The predictions of the new description are in good agreement with data from a series of single and multistep stress-relaxation experiments done in uniaxial extension on an ethylene-hexene copolymer. (page 31)

- An industry workshop on polymer composite processing was held with attendees representing users, fabricators, and suppliers of composites in the automotive, electronics, aerospace, and other industries. The workshop identified the generic processing methods likely to be of most interest to industry in the future and the scientific and technical barriers that hinder the implementation and effective use of these methods. (page 42)

- By varying the processing parameters, the molecular structure and toughness of a model epoxy system were modified. For a given composition, the toughness was found to correlate with the compositional fluctuation measured by small angle x-ray scattering. These compositional fluctuations can be controlled by changing the processing parameters so that optimum toughness in the single phase region can be obtained. (page 46)

- A new technique to measure the resistance of polymer resins to interlaminar crack growth in their composites was developed. This test uses a thin adhesive bond between metal adherents to simulate the constraint on the resin deformation produced in the composite by the fibers. Preliminary results shown an excellent correlation between fracture energies obtained in the adhesive joint test and experiments using composites. The new method has the advantages of easy fabrication, small quantities of resin required, and no fiber bridging problems. (page 51)

- A new procedure of obtaining the temperature, composition, and molecular weight dependence of the free energy of mixing for polymer blends has been established. This procedure which integrates the experimentally obtained interaction parameter, χ, with theoretical calculations to obtain a parameterized free energy function of mixing, has been demonstrated by using a binary polymer blend of polystyrene/poly(vinylmethylether). Spinodal and cloud point curves have been generated and found to compare favorably with experiment. (page 57)

- The use of crosslinks between unlike chains in a blend to increase compatibility has been studied by a SANS technique. Blends of polystyrene/poly(vinylmethylether) subject to radiation dosage of 125 MRad have shown an increase of the single phase region of over 250°C. (page 58)

- In the study of spiro orthocarbonate monomers capable of polymerization with an expansion in volume, a novel monomer was prepared which exhibits reactivity comparable to conventional methacrylate monomers and high ring-opening efficiency at near ambient polymerization conditions. (page 69)

- A novel dental restorative, a hybrid cement-composite, has been developed in order to overcome the propensity of conventional glass-ionomer cements to brittle fracture during wear from occlusion. The restorative involves the usual hardening of a commercial glass ionomer cement along with the polymerization of a water-soluble monomer (e.g. hydroxyethyl methacrylate) incorporated in the system to provide toughening. *In vitro* tests revealed good wear resistance, excellent oral-environmental resistance, and no catastrophic failure during wear. (page 64)

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
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Blair, William R.	o Ultratrace metals speciation o Biotransformation of metals o Polymer analysis by size exclusion chromatography o Environmental durability of coatings
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Bowen, Rafael L.*	o Adhesion o Dental composites o Biocompatibility
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Briber, Robert J.	o Structure and morphology of polymers o Electron microscopy o X-ray scattering
Brinckman, Frederick E.	o Environmental metal transport o Organometallic chemistry o Biological mediation of surface chemistry o Ultratrace metal speciation and particle biogenesis o Molecular structure-activity relationships
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†Guest Scientist

Bur, Anthony J.	o Dielectric properties of polymers o Fluorescence monitoring of polymer processing o Piezoelectric, pyroelectric polymers o Polymeric transducers
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Fowler, Bruce O.*	o Laser Raman structural analysis of calcium phosphates
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Gregory, Thomas M.*	o Calcium phosphate compounds o Surface chemistry

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Misra, Dwarika N.*	o Surface chemistry o Adhesion o Chemisorption
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Muller, Robert*	o Denture base materials o Soft liners

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Parks, Edwin J.	o Macromolecular organometallic chemistry o Metals imaging in coatings o Biological transformation of carbohydrate materials o Archival preservation
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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
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Takagi, Shozo*	o Crystallography o X-ray diffraction o Calcium phosphate compounds
Takahashi, Yoshiaki†	o Polymer Rheology o Block copolymer o Polymer synthesis and characterization
Tesk, John A.	o 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
Trout, Todd, K.	o Photoactive organometal-chelate chemistry o Diffuse reflectance/microscopic epifluorescence o Spectrophotometry o Element-specific microscopic epifluorescence
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Verdier, Peter, H.	o Polymer solution properties o Polymer chain dynamics in solution o Statistical analysis of data o Error estimation o Computer simulation of polymer chain dynamics
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Wu, Wen-li	o Neutron and x-ray scattering o Electron microscopy o Mechanical behavior of polymers and composites
Zapas, Louis J.	o Continuum mechanics & Rheology o Non-linear mechanical behavior of polymers o Static fatigue of plastics o Finite elasticity (rubbers)

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ELECTRICAL PROPERTIES

The goal of the Electrical Properties Group 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 or new applications or to entirely new polymer systems. 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, electro-optic measurements on specially synthesized materials, and magnetic properties of superconducting ceramic/polymer composites.

The measurement of dielectric constant and dielectric loss as a function of frequency and temperature has long been used to probe the molecular motions in polymers. Development of a time domain dielectric spectrometer at NIST has extended the ability of these measurements to follow dielectric properties which evolve with time, since data for a wide frequency range can be obtained in an interval of time comparable to the reciprocal of the minimum frequency of interest. 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 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. Use of the technique to measure the electric field - induced alignment of polar molecules dissolved in a polymer matrix is being explored.

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. Also, we are frequently called upon for technical information in this area by companies interested in developing applications for these polymers. Commercial interest is growing in copolymers of vinylidene fluoride with trifluoroethylene or tetrafluoroethylene because of ease in processing for ferroelectric properties and the Curie temperature which varies with composition. The variation of electrical properties with composition, thermal history, and morphology in these polymers is being studied.

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

FY 88 Significant Accomplishments

- The ability to obtain dielectric data in the time domain which can be transformed to encompass frequencies from 10^{-4} to 10^4 Hz has proven to be useful for detecting changes in cable insulation which has been exposed to heat and gamma radiation. This ability to follow the evolution of dielectric properties which was reported previously for monitoring the cure of thermosetting resins in composites is now being extended to monitor the firing of ceramic powders.

- In the design of polymers for nonlinear optics, diacetylene monomers which undergo multiple transitions to liquid crystalline states prior to melting have been synthesized. Thermally activated polymerization has been shown to occur not only in the solid state but also within the liquid crystalline states, with an activation energy of only 40% of that in the solid state. Furthermore, the resulting orange-colored polymer retains much of the long-range order present in the liquid-crystal precursor.

- Composites of $YBa_2Cu_3O_{7-x}$ superconducting powders dispersed in polyvinylidene fluoride have been prepared and shown to have the expected diamagnetic properties essential to applications involving levitation at temperatures below the critical temperature of 92K. The polymer matrix provides processability at elevated temperatures, flexibility at room temperature, and a chemically inert environment for the imbedded particles.

Automated Dielectric Measurements

F. I. Mopsik

The Time-Domain Spectrometer for measuring dielectric relaxation has been used to examine a wide variety of problems. This instrument, which was developed at NIST, carries out measurements in the frequency range from 10 kHz to 0.0001 Hz by measuring the charge response of a dielectric to an applied voltage step for times from 10μs to 3000 s and performing a numerical transform on the data. The sensitivity, accuracy and extremely wide frequency range has led to the commercialization of this instrument by IMASS, Inc. Hingham MA and the first units have now been introduced to the market. Areas in which the instrument has been used are described below.

Process Monitoring

Previous work has shown great promise for the use of dielectric loss measurements to monitor the cure of epoxy resin systems used in the production of composites. In particular, for amine and imidazole based resin systems, the changes during cure were very large, easy to characterize, and comparable to other techniques used to study the evolution of the cure. Of notable significance was the ability not only to follow the gelation of the resin, but also to follow the changes in the resin well past this point.

Epoxy resin systems are not the only type of resin being used. A peroxide-catalyzed styrene resin system was measured to see how well a less conducting system could be monitored. This is a short curing-time resin used in the automotive industry. The results showed that this resin system also can be easily followed even though the resin can self-heat to the point of thermal runaway. This thermal runaway prevented a reliable comparison with mechanical and DSC measurements but measurements of the self-generated temperature rise in all the instruments involved indicated that the degrees of cure determined by the methods are consistent.

In another application of process monitoring, in cooperation with the Office for Nondestructive Evaluation and the Ceramics Division, the use of dielectric relaxation data to study the processing of ceramics was begun. The first studies were made on a yttria-stabilized zirconia ceramic as a function of partial firing conditions. The data were evaluated for sensitivity to density and possible grain boundary effects. In addition, the validity of impedance spectroscopy using complex resistivity and its connection with the more common presentation of data in the complex dielectric constant plane was started. The first results on this particular ceramic did show promise and pointed out the desirability of different forms of data presentation in these systems. However, the great variability of the material parameters on composition precluded further conclusions. A follow-up study for alumina based ceramics is planned to expand on these results.

Reactor Cable Insulation Testing

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

Following previous results on cables obtained from the Shippingport reactor, additional samples were obtained that had been exposed to a known dose of 25 Mrad from various sources. The insulation was all identified as cross-linked polyethylene but the samples clearly differed in terms of appearance and additive content. All samples were measured in both the original, unirradiated state and the irradiated state. A reference temperature of 50°C was maintained for all measurements.

The materials in their untreated states varied quite extensively in their loss over the measured frequency range of 10^{-3} to 10^{4} Hz. The filled samples all had higher loss while the unfilled samples had extremely low loss. Upon irradiation, the filled samples showed much smaller changes then the unfilled ones. In particular, one of the filled samples showed virtually no change at all while the unfilled ones showed very large values for radiation-induced conductivity and signs of degradation. These results illustrate the great sensitivity of radiation damage in polymers to additives and the need for monitoring of actual cables.

Poling Mechanisms in Polyvinylidene Fluoride - Trifluoroethylene Copolymers

As part of a study to determine the mechanism for erratic poling behavior in polyvinylidene fluoride - trifluoroethylene copolymers, the dielectric loss spectra for 70/30 and 80/20 composition copolymers was measured. This was done to see if possible internal charge build-up was responsible for the behavior. Since the dielectric properties of pure polyvinylidene fluoride had already been determined and poling characteristics were normal, it was felt that excess charge carriers in the copolymer should be easily found.

All the copolymers showed similar behavior. Unlike the homopolymer no relaxations centered at either 10 Hz or 0.1 Hz were found. The very low frequency loss was quite similar to that of the homopolymer and did not change with temperature in a manner consistent with conduction. No significant correlation could be found with degree of difficulty of poling. Comparison with poling experiments indicated that a charge mechanism was inconsistent with the changes in poling behavior. Subsequent investigations have shown large changes in coercive fields associated with initial crystallization conditions.

Plasticization

A guest worker from Johns Hopkins University is using the spectrometer to measure the plasticization of polymers by gases by studying the shift in the relaxation spectra of the polymer. A compatible cell has been designed and the first preliminary measurements carried out.

Thermal Pulse Measurements of Polarization and Space Charges

A. S. DeReggi, G. T. Davis, F. I. Mopsik, and S. C. Roth

Space Charge in Polymer Films

The distribution of electric charge or polarization across the thickness of various polymers continues to be of interest within the Polymers Division and in many other laboratories worldwide. The laser thermal pulse facility used at NIST to determine polarization distributions has undergone evolutionary developments to meet the specific requirements of changing tasks and to remain state-of-the-art in the face of intensive work elsewhere on complementary measurement methods using acoustical rather than thermal pulses.

Under the sponsorship of the Defense Nuclear Agency, NIST has assisted Hy-Tech, Inc. of Radford, VA in clarifying the charging behavior of 8 μm-thick Kapton films. These films are used by Hy-Tech in simulating the electrical behavior of many polymers used as structural components of spacecraft. Polymers gradually charge up in a space environment (due to charged particles in Van Allen belts, or cosmic rays) and can suddenly discharge with deleterious effects on the spacecraft function if exposed to the X-ray-rich electromagnetic pulse (EMP) produced by a nuclear event. EMP tests duplicating the conditions in a nuclear event are difficult to run and are extremely costly (the available

National facilities to conduct such tests are few and all operate at very low repetition rates of at most a few pulses per day). There is interest in finding out if the electrical behavior of polymers can be simulated less expensively by using electron beams for charging and UV-rich rather than X-ray rich electromagnetic pulses for discharging. A considerable amount of fundamental research is required to address the mission-oriented concerns of the sponsor and contractors. Samples charged at Hy-Tech have been sent to NIST for measurement using overnight mail to reduce the time between electron beam exposure and measurement. The quantity of charge measured for fixed beam conditions depends on the beam exposure time, on the voltage across the sample, and on the time between exposure and measurement. The distribution of remanent charge depends on beam energy, the effects of the irradiation on material properties and on the charge transport kinetics. The measurements performed so far using 45 kV electron beam energy, few nA/cm^2 beam current, and a few hours charging times indicate remanent charge in the tens of nC/cm^2 which is easily measured. However, our understanding of the mechanisms is still only qualitative. One objective of the research is to correlate the behavior of the charging current, which depends on the irradiation time and on the voltage across the sample, with the remanent charge measured afterwards. A second objective is to characterize the charge remanance time which depends on the radiation-induced conductivity. A third objective is to measure the changes in remanent charge induced by voltages applied during the post-irradiation period of relatively high electrical conductivity.

Polarization in VF$_2$/TrFE Copolymers

The thermal pulse facility has also proven useful in characterizing the electric polarization behavior of copolymers of vinylidene fluoride and trifluoroethylene which depend in unexpected ways on the thermal treatment. Specifically, moderate heating of a sample in a ferroelectrically soft state renders it highly resistant to poling or to ferroelectric switching by an applied electric field, while heating it above its Curie temperature restores softness to the ferroelectric state. We have demonstrated that this unique behavior can be exploited in the fabrication of biomorphic actuators and of novel, layered composite, ferroelectric memory devices. Layered composites with two or three layers were prepared using layers of either of two possible copolymer compositions which were chosen to have different and far apart Curie temperatures. One composition was 80% VF$_2$-20% TrFE with a Curie temperature of 140°C. The other composition was 65% VF$_2$-35% TrFE with a Curie temperature of 80°C.

Judicious choice of the sequence of electrical and thermal treatment of a particular layered composite produced a variety of polarization combinations for the various layers. These combinations were effectively characterized by measuring the polarization distribution across the composite using the thermal pulse technique. In the case of a three-layer composite with the inner layer having a high T_c and the outer layers having a low T_c, the following polarization states were produced. First, the entire composite was poled and it was verified by thermal pulse measurements that the polarization was nominally uniform (the same in magnitude and direction for each component layer). Second, the composite was heated to 100°C (which is between the two Curie temperatures). Thermal pulse measurements showed that only the inner layer retained polarization, the outer layers having lost their original polarization as a result of heating to 100°C. Finally, the composite was reverse poled. Thermal pulse measurements confirmed that the outer layers had reversed polarization relative to the original and showed also that the inner layer had not switched but instead had retained its original polarization. That and related experiments have cleared up the poling behavior of the ferroelectric VF_2-TrFE copolymer. We have shown that one type of thermal treatment is necessary for poling to nominal saturation polarization. Remanent polarizations of 9 $\mu C/cm^2$ have been achieved for samples with 80% VF_2, 20% TrFE which have unusually sharp hysteresis loops among ferroelectric polymers. We have also shown that another type of thermal treatment increases the stability against electric-field switching of the polarization of a poled sample. We have demonstrated that bimorphs can be constructed using layered composites. We anticipate that, by inducing specific combinations of polarization states in a multilayer composite by appropriate electrical and thermal treatment sequences, it will be possible to construct devices with novel transducer or memory properties.

Ferroelectric Polymers

G. T. Davis, A. S. DeReggi, F. I. Mopsik, and S. C. Roth

Small Area Ultrasonic Probes

Since the initial NIST work on spot-poled piezoelectric polymer membrane hydrophones a decade ago, such hydrophones have gained wide acceptance for probing ultrasound fields. The main benefit of using a polymer as the piezoelectric material in ultrasonic applications, notably in medical diagnostics where the ultrasonic medium is water, a saline solution or living tissue, is that the probe is nearly acoustically transparent and hence allows probing the ultrasonic field without disturbing it significantly. The common diagnostic frequencies for a long time have been in the low MHz range (3.5 MHz commonly) but current imaging systems use somewhat higher frequencies (7.5 MHz typically) and ophthalmic systems use still higher frequencies (10-15 MHz). For the low MHz range, typical active diameters have been around 1 mm. The trend for increasing operating frequencies, together for the desirability for the active areas to be small compared to the ultrasonic wavelengths require smaller active diameters. The American Institute for Ultrasound in Medicine, and the ultrasonics industry through its representative bodies, the National Electrical Manufacturers Association and the International Electrotechnical Commission have published guidelines for choosing the size of the active region of ultrasonic probes. A reduction of the active diameter from 1 mm to 100 μm would represent a significant improvement for the industry.

In collaboration with the U.S. Food and Drug Administration, Center for Devices and Radiological Health, the Polymers Division is investigating novel techniques for spot-poling polymer membrane hydrophones. Needle-ball electrode configurations have been used successfully to obtain active diameters in the range 200-300 μm for 12 μm-thick polyvinylidene fluoride. These diameters are significantly larger than the diameter of the needle electrode suggesting that fringing effects set an electrical lower limit to the achievable active diameter. Related research on promising alternative materials, notably a copolymer of vinylidene fluoride and trifluoroethylene suggests that further reductions of the active diameter may be achievable using local thermal treatments applied to the desired active area. This related research shows that the coercive field (the ferroelectric switching field required to pole the material or reverse its polarization) depends on the thermal treatment. Annealing a small spot on a sheet previously quench-crystallized is expected to result in the spot having a much smaller coercive field than the rest of the sheet. Poling would occur selectively where the spot heating occurred. Concurrently, promising methods of spot heating involve using a suitably focussed pulsed laser beam.

Improvements in measurement techniques for characterizing the smaller active areas are being sought. The trend toward increasing operating frequencies to the range of 10 MHz will also require extending measurements of the acoustical properties of ferroelectric polymers to this region.

High Power Generators

For specialized applications, the ferroelectric polymers offer systems capable of delivering small amounts of energy associated with changes in electrical polarization at a high rate and hence can be made into potentially promising high power generators. In collaboration with Chronos, Inc. the Polymers Division is investigating means of rapidly heating ferroelectric polymers by means of a pulsed laser to produce fast pyroelectric signals.

Initial experiments employed a dye dispersed throughout the polymer which absorbed in the energy region of a pulsed dye laser. The pyroelectric response combined with the loss of polarization at the Curie temperature over a time scale of 1μs results in power outputs of up to 45 GW/kg.

High T_c Superconductor-Low Tg Polymer Composites

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In a number of magnetic applications of high T_c superconductors, such as levitation, electrical continuity throughout the material is not essential for the function. In such applications, composite materials consisting of powdered high T_c superconductors incorporated into a polymer binder may play an important commercial role because of the processing advantages they share with polymers. They can be extruded into ribbons and sheets or injection-molded into a variety of complex three dimensional objects.

In collaboration with personnel in the Ceramics Division and Metallurgy Division, we have succeeded in preparing stable composites using polymers with the requisite thermal, mechanical, electrical properties and chemical inertness. Current research is aimed at understanding the relationship between the magnetic properties of the composite and those of its components. An important issue being addressed is whether an effective composite magnetic permeability between 0 and 1 (susceptibility between -1 and 0) can be defined to allow magnetostatic calculations of magnetic fields inside composite shells. The superconductivity composite in an applied magnetic field is modeled by an assembly of fixed, aligned magnetic dipoles, where the separation between dipoles is large compared to the superconductor grain dimensions. This model is analogous to the Lorentz model in dielectrics and predicts a composite permeability which varies nonlinearly with superconductor volume fraction.

Magnetic susceptibility and magnetization versus magnetic field measurements as a function of temperature and superconductor fraction are being obtained. The dependence on superconductor-fraction measured so far are consistent with the predictions of the Lorentz model. However, the experimental errors in calibrating the measurements due to the shape of the specimens do not rule out other models.

Equipment has been procured to measure the shielding factor of the undiluted superconductor and of composites as a function of superconductor fraction. These measurements are expected to provide further clarification of the validity of the Lorentz model for predicting the magnetic behavior of a composite.

Nonlinear Optical Properties of Polymers

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Liquid Crystalline Diacetylene Monomers and Polymers

Within recent years, small organic molecules and polymer systems that incorporate delocalized π-conjugated electrons have received much attention because of their unique electronic properties. Much of this now centers around the transient response of these materials to high electric field strengths such as are associated with pulsed laser systems. From a technological viewpoint, these materials form the basis for the rapidly developing integrated and nonlinear optics industries. From a condensed matter physics viewpoint, these materials allow the investigation of photo-induced structural changes arising from exciton generation in one-dimensional conjugated structures.

As potential elements within nonlinear optical (NLO) devices, polydiacetylenes, (PDA's) combine a large number of important primary and secondary properties which include a large non-resonant, third order susceptibility, picosecond scale switching times, phase matching, film flexibility, and large dielectric constant to name a few. However, if NLO devices are to be fabricated, a larger macroscopic susceptibility must be achieved either by improving the intrinsic susceptibility, of the polymer or by increasing the density of conjugated units.

An approach to obtain large PDA films which is being pursued in our laboratory involves the synthesis and polymerization of unique diacetylene monomers which exhibit liquid crystalline (lc) phase behavior. This exploits a unique characteristic of diacetylene polymerization chemistry, i.e. the need for nanometer-scale organization of monomer for formation of high polymer to occur. Traditionally this has been achieved by conducting polymerizations within the monomer single crystal or in organized molecular monolayers such as are obtained by Langmuir-Blodgett techniques. Starting with liquid crystalline monomers, it is believed that single phase, macroscopic monomer phases leading to polymer of high optical quality can be obtained.

Another important purpose of this research is to expand our understanding of how nanometer-scale organization influences the polymerization of polydiacetylenes. Specifically, both intermolecular spacing between adjacent monomers and the angle of tilt of the monomer relative to the crystallographic c-axis are proposed structural factors that determine polymerization. Liquid crystals frequently exhibit polymorphism whereby each phase is characterized by an ever decreasing level of molecular organization with increasing temperature. Consequently, with a single liquid crystalline monomer, a variety of organized monomer phases can be obtained and structure-dependent polymerization can be examined. It is our belief that by understanding the latitude of molecular disorder which can be accommodated within a polymerizable diacetylene monomer lattice, greater flexibility is gained in molecular processing of the resulting polymer as a nonlinear optical material.

A number of novel diacetylene monomers, some of which exhibit liquid crystal phase behavior, have been synthesized within our laboratory. Broadly speaking, these fall within two material classes:

- Class A: monomers which exhibit liquid crystalline phase behavior and result in insoluble polymer, and
- Class B: monomers which do not exhibit liquid crystalline behavior but upon polymerization, are expected to yield side-chain liquid crystalline polymer architectures.

Within class A, the 1-OBOA, 1,6-bis[N-(4-oxybenzylidene)-4-n-octylaniline]-2,4-hexadiyne, monomer has been most thoroughly studied within the past year. Elevated temperature small angle x-ray scattering (SAXS) studies in conjunction with optical microscopy and differential scanning calorimetry (DSC) of the monomer show at least two and perhaps three different mesophases of which two are smectic. Within the crystal($T \leq 133$°C) and the smectic mesophases, SAXS data indicate that the monomer is tilted relative to the layer line at approximately 30°. Analysis of the wide angle x-ray scattering is incomplete so assignment of intermolecular d-spacings between diacetylene monomer units is still pending.

Kinetic measurements derived from DSC data following the thermal induced liquid crystal phase (lcp) polymerization of 1-OBOA indicate first order disappearance of monomer over much of the polymerization. A thermal activation energy, E_a, for polymerization initiation of 155kJ/mol is found. This is much larger than the 92 kJ/mol. energy of activation for thermally polymerized 1,6-bis(4-toluene sulfonate)-2,4-hexadiyne monomer. Preliminary kinetic data obtained within the crystal phase indicates a larger energy of activation, about 295 kJ/mol. Further experiments at lower temperatures are now being conducted.

Models derived by Baughman and Schmidt both predict a narrow range of intermolecular distances between diacetylene groups and monomer angle within the unit cell for polymerization to take place. Kinetic data in conjunction with x-ray structural data are being combined to determine whether these models for diacetylene polymerizability in the crystal phase can be extended to include the liquid crystal phase.

FTIR and elemental analysis of thermally polymerized 1-OBOA are consistent with the theoretical structure. No chemical degradation of the benzylidene side chains is seen after polymerization within the lc phase as shown by the mid-infrared region data. Micro elemental analysis shows the mole fraction of C, H, N, and O agrees within 0.00%, 0.55%, 0.11%, and 0.02% respectively with theoretical values for 149°C/8hr. vacuum polymerized polymer. Poly(1-OBOA) is insoluble in common solvents and is deeply orange colored.

SAXS experiments during and after polymerization have demonstrated a number of important points. With polymerization, the sharp small angle reflection representative of the monomer {001} is seen to decrease and eventually disappear. This is replaced by a broad, strong reflection whose Q-vector increases with conversion. Consequently, poly(1-OBOA) obtained via a lcp polymerization is shown for the first time to exhibit a lamellar-like micromorphology. Microscale sheet-like ordering is therefore conserved with lcp polymerization. Whereas the SAXS data for the monomer represents the layer thickness, the data for the polymer represents the distance between polymer chains or sheets.

Wide angle x-ray scattering experiments for determining the organization within the individual polymer layers are being planned for this year. It may be envisioned that depending on the particular microphase within which the monomer is first polymerized, either three dimensional anisotropic or two dimensional isotropic structures may result.

Guest-Host Systems

Polymer films can be made to exhibit large second order electric field coefficients by incorporating small molecules of large polarizability, followed by preferential alignment in an electric field. Cooling below Tg retains the molecular alignment in the case of amorphous polymers and large internal electric fields resulting from preferentially aligned polar crystals induces alignment in the case of semicrystalline ferroelectric polymers. In addition to the useful second harmonic generating properties of such films, changes in the UV/vis absorbance and shifts in the absorbance maximum can be used as probes for internal electric fields in the polymers. Our initial studies have incorporated 2-methyl, 4-nitro aniline or 4-dimethyl amino, 4′ nitro-stilbene in a vinylidene fluoride-trifluoroethylene copolymer containing 25 mole percent trifluoroethylene. Preliminary data imply internal electric fields on the order of a few MV/cm which is consistent with previously published data and the polarization to be expected from the copolymer crystals.

POLYMER STANDARDS AND CHEMICAL PERFORMANCE

The goal of this task is to produce standard reference materials (SRM's) for the polymer industry; to develop measurement methods, data, and models for the control of polymer processing; and to carry out long-range research on polymer characterization and chemical performance properties of polymers.

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

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

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.

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.

A program has been initiated on bioprocessing and molecular characterization of organometallic materials in this task, as a result of the transfer of personnel to the Polymers Division. Investigations in this program involve the use of microorganisms and their metabolic products for upgrading, synthesis, recovery and degradation of materials, and the development of methods for monitoring biotic transformations of a variety of substrates. In addition, in response to the need identified by Congress, a new effort has been initiated to study biodegradation mechanisms of polymers.

FY 88 Significant Accomplishments

- Two linear low density polyethylenes used in gas piping (one with, and the other without pigment) have been issued 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.

- Certification measurements have been completed for a poly(methyl methacrylate) Standard Reference Material, SRM 1487. Produced with partial support from the Navy, this SRM will be used for quality control of antifouling paints and as a calibrating material for the analysis of acrylic polymers. Material has also been obtained and work started on the first of two polyurethane Standard Reference Materials, produced with partial support from the Food and Drug Administration, which will help meet a growing need for better methods of characterizing polyurethane used in medical devices.

- A polymeric chromophore, which consists of polybutadiene labelled with fluorescently active anthracene, has been synthesized and characterized. Since its number average molecular weight, 12,000, is above the entanglement molecular weight, this polymer can be used to monitor polymeric behavior such as non-Newtonian viscosity and molecular orientation.

- The results of mixing experiments, carried out using a fluorescence microscope, give quantitative support to our hypothesis that fluorescence can be used to monitor the quality of the mixture of a two component compound.

- A sensor has been designed to measure velocity, velocity gradient, and flow instabilities. The sensor operation is based on fluorescence recovery after photobleaching. A mathematical model to describe its behavior has been formulated.

- Significant removal of phosphorus from an industrial iron ore concentrate by metabolic products of microorganisms was shown. This treatment offers a potential method for upgrading of domestic iron ore reserves with elevated levels of phosphorus, providing higher quality raw material for steel making.

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

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

- Microbiological films were shown to significantly accumulate tributyltin, the active biocidal agent in many new antifouling coatings. This information provides insights into the mechanism of antifouling activity of these coatings and suggests that such coatings could be designed to have very low biocide release rates, lessening their environmental impact.

Standard Reference Materials

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

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.

We are producing 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. These SRM's are not the usual commercial polyurethanes, but rather are model compounds to which the usual techniques for determining molecular weights of homopolymers can be applied. We are also developing methods for estimating compositional variation in polyurethanes, both for checking our own SRM's and for investigating the range of variation in commercial polyurethanes. During FY 88 we have obtained material for the first polyurethane SRM, and have begun measurements leading to its certification.

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 is considerably higher in molecular weight than any of the polyethylene SRM's now available. Such a standard is 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, has been certified. The other two melt flow rates are 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. The molecular weight distribution of both materials has been estimated from gel permeation chromatography and is given as supplemental information on the certificate.

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 produced. The number-average molecular weights of SRM's 1488 and 1489 were 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 have been completed.

Polyolefin Melt Flow Rate Standards

Melt flow rate (or melt index) measurements are used in specification of polymers in the polymer industry. NIST SRM's with certified melt flow rates are used to check equipment stipulated by the ASTM D-1238 voluntary standard. Current NBS polymer SRM's all have melt flow rates of less than 2 g/10 min. Additional polyolefin standards are needed for melt flow rates higher than 2 g/10 min.

A polyethylene SRM with a melt flow rate of 5 to 7 g/10 min is currently in production. This work is supported by OSRM.

A polypropylene with a melt flow rate of about 12 g/10 min is being considered for certification using ASTM Method D-1238 condition 230/1.2. The need for this material has been established through consultation with the members of the subcommittee of ASTM D-20 in charge of Method D-1238. Support for this work is currently being negotiated with a group of polymer companies represented on the ASTM subcommittee.

Ore Bioleaching Standards

More effective bioprocessing designs and improved strains of bacteria are sought for commercial ore bioleaching. These developments are limited by lack of understanding of the underlying mechanisms and the factors which limit the rate of microbial ore dissolution. In particular, data intercomparison is difficult because standard materials and protocols for conducting ore bioleaching assays do not exist. We are working with OSRM and ASTM to develop standards for metal ore bioprocessing.

A source of domestic pyrite ore material suitable for bulk SRM or research material production has been identified and tested. The material has been shown to exhibit reproducible iron bioleaching rates following NIST-developed test procedures. These novel OSRM-supported results provide critical data necessary for a proposed FY 89 prototype SRM production and international bioleaching measurement intercomparison with ASTM.

Polymer Processing

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Work during FY88 has focused on five areas: the design of experiments to measure fluorescence anisotropy and non-Newtonian viscosity as a function of shear rate; the chemical synthesis of a polymeric chromophore which is being used in experiments to measure fluorescence anisotropy; the development of a mathematical model to describe fluorescence recovery after photobleaching and its relationship to velocity and flow characteristics; measuring the quality of mixing of a two component material using a fluorescent microscope; and, negotiating with industrial laboratories for the purpose of carrying out collaborative research and developing programs to solve polymer processing problems of mutual interest.

Fluorescence Anisotropy and Synthesis of a Polymeric Chromophore

Fluorescence anisotropy measurements are being carried out using two pieces of equipment, a capillary flow apparatus and a Weissenberg rheometer. The capillary flow apparatus is used in conjunction with a commercial fluorimeter so that fluorescence and viscosity can be measured simultaneously. A capillary is positioned vertically in the sample chamber of the fluorimeter and the shear rate experienced by the specimen is controlled by adjusting the pressure applied at the top of the capillary. We have recently completed optical instrumentation of the Weissenberg rheometer and are using it to carry out fluorescence and rheological measurements. The range of shear rates covered by these instruments is approximately 10^{-2} to 10^{2} s^{-1}.

Fluorescence anisotropy measurements are being conducted on a low molecular weight polybutadiene specimen doped with a polymeric chromophore. The polymeric chromophore, which has been synthesized in our laboratory, consists of polybutadiene tagged with fluorescently active anthracene so that the anthracene is situated at the center of the polymer chain. Infrared and gel permeation chromatography indicate that anthracene has been placed in the central position of the polymer chain and that the resultant number average molecular weight is approximately 12,000 as expected.

Our working hypothesis for the anisotropy experiments is that, for a non-Newtonian fluid, the fluorescence anisotropy increases (and the viscosity decreases) with increasing shear rate, and that the underlying cause of this effect is molecular orientation. The fluorescence anisotropy experiment is designed to measure this molecular orientation. In our first experiments we have tested the converse of this hypothesis, i.e., for a Newtonian fluid, fluorescence anisotropy is constant (as is the viscosity) as a function of shear rate. Low molecular weight polybutadiene, M_n = 2800, which was doped with the tagged polybutadiene (10^{-4} molar concentration), was observed to be Newtonian and to have constant anisotropy in the shear rate range 10 to 80 s^{-1}. We conclude that, within the sensitivity of our measurement, molecular orientation of the tagged polybutadiene does not occur in this low molecular weight polybutadiene. Experiments using non-Newtonian polybutadiene, M_n = 24,000, are now in progress.

Velocity and Flow Model

A sensor to measure velocity, velocity gradient, and wall slip near the wall of a processing machine was designed and a mathematical model to describe its behavior was formulated. The sensor operation is based on fluorescence recovery after photobleaching. The design consists of an optical fiber which is threaded through the wall of a processing machine and is flush with the inside wall. Polymeric material containing a photobleachable dye flows passed the end of the optical fiber and the fluorescence properties in a defined region at the end of the fiber are observed. At a given instant in time, the dye in the probed volume is photobleached by a short pulse of ultraviolet radiation. As function of time, fluorescence intensity recovers as fluorescently active material flows into the probed volume. In the model, we analyze this fluorescence recovery and derive a functional form for intensity versus time. From the equations, it is possible to distinguish between laminar flow and wall slip and, in the case of laminar flow, to obtain values for velocity and velocity gradient. Experiments to test this model will be carried out in FY89.

Measurements of the Quality of Mixing

Previous experiments carried out in this laboratory demonstrated the feasibility of using fluorescence intensity fluctuations to monitor the quality of mix of a two component mixture. This mixture consisted of polybutadiene doped with an active chromophore (coumarin 30) and 14 μm grain size aluminum oxide. Using a laboratory size mixer, fluorescence measurements were made by directing a laser light beam to the glass wall of the mixer and monitoring the fluorescence from material as it passed through the probe volume of the laser beam. We observed that fluctuations in fluorescence intensity decreased with mixing time and became uniform with time at the end of mixing. Our hypothesis is that fluorescence intensity will be constant with time when a uniform spatial distribution of material occurs. While the initial experiments established qualitative support for this hypothesis, we have also carried out a quantitative study of mixing. The quantitative data are being obtained using a fluorescent microscope to measure the near neighbor distance between particles and the standard deviation of this distance as a function of mixing time, fluorescence intensity fluctuations, and optical density. We have established a correlation between fluorescence intensity and optical density over a range of mixing conditions and a correlation between near neighbor distance and fluorescence fluctuations.

Interactions with the Polymer Processing Industry

Considerable effort was exerted for the purpose of increasing the amount of industrial interaction and participation in our polymer processing program. A news release, which was issued from the NIST Public Relations Division, generated over thirty responses from major polymer processing companies. We have responded to each request and are in the process of active negotiation with a half dozen companies concerning the establishment of research associateships. Additional industrial contacts are being developed via the IST Intelligent Materials Processing Workshop to be held on August 31, 1988.

Molecular Characterization

F. W. Wang, C. M. Guttman, A. J. Bur, P. H. Verdier, and R. E. Lowry

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.

We have synthesized the poly(amide-acid) polymer, deposited thin films of the polymer on silicon wafers, and characterized the formation of polyimide in these films by fluorescence spectroscopy. We are also using FTIR and mass spectrometry to characterize the chemical changes that occur during thermal treatment of these thin films.

Fluorescence Studies of Polymer Solutions

Fluorescence quenching of dilute solutions of polymers allows one to study the shape of the polymeric chain in dilute solutions and the chain's interactions with itself, with other chains, and with solvent. 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. Currently theoretical studies using renormalization group and scaling methods are being used to establish the relationship between the fluorescence properties of isolated chains or two chains in solution and other chain properties. Monte Carlo simulations of single chain and two chain properties are being carried out to check the renormalization group and scaling theories. 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 dynamical 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, 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. More realistic theoretical treatments of polymer melts and elastomers, which must start with more realistic treatment of the dynamical behavior of the individual chains, will lead to more efficient processing and better fabricated end products. A major shortcoming of the present theory is its inability to treat excluded volume and chain entanglement effects in a realistic way. Present work is aimed primarily at the study of these effects, using a combination of analytical and computer simulation techniques. The simulation results provide data on simple model systems and serve to guide the development of better theoretical treatments.

Present efforts in this project are in two areas. The first of these is a study of the effects of changing the chain move rules upon relaxation behavior, in an attempt to resolve discrepancies between results obtained by different groups using different model systems. The second is a series of studies of size and knotting effects in systems of closed-ring chains. Although these are primarily studies of equilibrium effects, dynamical models are needed to carry them out for closed-ring systems. The results of this work may help to explain anomalies found in experimental data on such systems.

Failure of Latex Barrier Films

The failure of latex barrier films is of both commercial and medical interest. Regions with low local crosslink density may be expected to fail under certain loading conditions. We are studying the change in the crosslinked density across the film by measuring the change in local swelling using fluorescence technique.

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

Bioprocessing

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Work in this subtask is investigating the use of microorganisms and their metabolic products for upgrading, synthesis, recovery and degradation of materials and in developing measurement methods and standards to better understand mechanisms and rate limiting factors involved in these processes.

Steel Research Program

Microbiological metabolic products are being evaluated as potential agents for upgrading the quality of raw materials used in steelmaking including iron ore and simulated steel scrap. Domestic reserves of iron ore often contain elevated levels of phosphorus which causes brittleness in steel. Low cost routes are sought to remove phosphorus in ore concentrates. However, to date industry has not been successful in achieving effective low cost processes. We isolated a phosphorus dissolving fungus and identified metabolic products capable of solubilizing phosphorus minerals. Tests with U.S. industrial iron ore concentrates showed the bioproducts, consisting of oxalic acid and other organic acids, rapidly (<10 min) removed over 50% of phosphorus from the ore and potentially offer a novel bioprocess for domestic iron ore beneficiation. More detailed evaluation of biological dephosphorization and potential on-site scale-up testing with Cleveland Cliffs Iron Co. and Michigan Technological University is planned.

Also under evaluation is the concept of using low energy routes for metal reduction. We investigated novel pathways to metal reduction using microbiological metabolites. Bioreduction of gold and other precious metals to pure metallic microparticles by volatile metabolic products was demonstrated. The reactions involve the production of methylated metabolites which react with the metal ions in water to form methylmetal intermediates. These undergo reductive demethylation, forming pure metal particles. The particles were studied by electron microscopy-energy dispersive x-ray microanalysis for morphology and purity. The work attracted an invitation from the Metallurgical Society and the American Institute for Mining Engineering to present a talk on the subject at the upcoming Symposium on Biotechnology in Minerals and Metals Processing. Several platinum group metals and catalyst industrial firms have indicated collaborative interest.

Bioprocessing of Metals: Mechanisms and Methods

The removal of metals from solution is an area in which biotechnology is also making a contribution in waste clean-up and metal recovery. Applications to date are limited to a very few metals. The bioaccumulation of gallium by microbial cells and gallium binding by exocellular biogenic iron chelators, or siderophores, was demonstrated as part of an Air Force-supported project to develop novel processes for gallium recovery to assure domestic supplies of this critical element. In recent years there has been little or no domestic Ga production. Ga occurs with Al but its separation is difficult and costly. Our research may provide new options for Ga recovery using the extraordinary specificity of certain biomolecules. Center for Analytical Chemistry scientists are collaborating in this research. They isolated and characterized the bacterial siderophore and are studying its Ga binding properties by NMR.

Non-destructive neutron and x-ray scattering and microscopic methods were developed to measure the bioaccumulation of metals. The application of small angle neutron and x-ray scattering techniques to characterize metal particles in and on living cells was successfully demonstrated, and conditions necessary to conduct kinetic metal bioprocessing experiments were established. These novel methods now permit investigation of the factors affecting metal particle formation rates in microorganisms. Epifluorescence microscopic imaging (EMI) methods in combination with fluorogenic ligands were used to demonstrate bioaccumulation of yttrium by bacteria and aluminum by plant material. The metal-fluorescent ligand complex permits detection of metals on surfaces with spatial resolution. These demonstrations illustrate the potential of the method for trace monitoring of metals bioprocessing. The work with plant material has attracted the interest of USDA scientists who are studying plant-aluminum toxicity and need a method to reveal sites of Al uptake.

Biotechnological processing of metals often employs microorganisms that posess metal resistances, as such organisms often transform metals in potentially useful ways (precipitation, redox reactions, volatilization). In particular, metal detoxification by microorganisms may potentially be applied to the treatment of toxic wastes. In collaboration with Prof. F. Baldi of the University of Siena, Italy, we studied the mechanism of chromium (VI) resistance in a chromium-resistant yeast isolated from tannery wastes. We showed that the mechanism of resistance was the exclusion of Cr from the cells. We also characterized mercury resistance and biotransformations by aerobic bacteria isolated from Italian cinnabar deposits. Hg resistance involved reduction to volatile elemental mercury. We also showed that biomethylation of mercury is not a mechanism of mercury resistance.

Bioprocessing for Upgrading of Fuels

The increasing concern over air pollution by combustion of fossil fuels has led to increased research on methods for precombustion removal of sulfur from coals. Better understanding of the molecular forms of sulfur in coal is needed as are processes for removing organic sulfur. The desulfurization of coal by extremely thermophilic bacteria (100 °C) was demonstrated in a joint NIST-Johns Hopkins University project supported by the Electric Power Research Institute. A novel approach using bioreduction, as opposed to oxidation, was taken as a route of desulfurization. The extreme thermophiles showed extremely rapid sulfur reduction rates. The use of microorganisms to bioassay sulfur species in coal was also demonstrated. These data provide information on the types and accessibilities of forms of sulfur in coal and also provide novel processing options for coal beneficiation.

Biodegradation of Materials

The effects of microorganisms on the fate of materials in service environments was investigated, including tributyltin-based antifouling coatings and biodegradable polymers. Tributyltin (TBT)-based antifouling coatings are effective in preventing hard (i.e. barnacles) fouling on ship hulls. However, recent legislation in several states bans or restricts the use of ship antifouling paints containing TBT biocide because TBT is toxic to non-target marine life which may encounter the material after it leaches from ships and drydock operations. Consequently, the development of effective antifouling paints with TBT release rates as low as possible is sought. However, the exact mechanism of TBT action on fouling organisms is not fully understood, particularly in relation to the microbial biofilms which form on TBT-painted surfaces immersed in seawater. We demonstrated the substantial bioaccumulation of TBT in microbial biofilms composed of organisms obtained from test panels coated with organotin antifouling coatings. There were no detectable degradation products (di- and monobutyltin species) in the biofilms or surrounding solutions. These results provide the U.S. Navy with data suggesting that the mechanism of antifouling action of tributyltin biocide may involve its concentration in microbial films, resulting in repulsion of hard fouling organisms (i.e. barnacles) from ship hulls. Consequently, antifouling paints with very low biocide release rates may be effective in antifouling protection while contributing minimal levels of toxicants to surrounding waters.

There has been rapidly increasing interest in the development of biodegradable plastics to reduce environmental pollution, both in terrestrial and marine environments. Definitions of biodegradability, and the associated measurement methods and standards will be needed as new plastic materials enter the market. Consequently, we acquired reportedly biodegradable starch-copolymer blends to determine the kinds of organisms which degrade these materials, the products of degradation and measurements which may ultimately be useful criteria for biodegradability. Our studies in this area have only just begun. However, we found that microorganisms specified for use in existing ASTM procedures for measuring resistance of polymers to biodegradation will degrade certain of these materials, as shown by their growth on the materials. Additional research will be conducted in the coming year with support of OSRM.

New Measurements and Predictors of Toxicity

Microorganisms were investigated as agents for novel measurement methods for ultratrace detection of toxicants and for validation of predicted toxicity of molecules based on their molecular structural properties. In a recently inaugurated collaboration with Technical Assessment Systems, Inc., their research associates have installed and demonstrated with NIST staff members the first applications of ultratrace biosensing of organometal toxicity by in vitro computerized multilaser spectrophotometry. A battery of genetically defined test microorganisms is evaluated for changes in morphology or growth upon exposure to a toxicant, providing a diagnostic response "fingerprint". We are correlating these responses with data obtained from conventional chemical speciation measurements to determine the specificity and sensitivity of the bioassay. The method may provide a more rapid, inexpensive, field portable measurement system for a variety of compounds.

Biomolecular Characterization - Inorganic Materials

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Work in this subtask includes development of improved or novel methods affording on-line or in-situ monitoring capability for inorganic, organometallic, and non-metallic substrates undergoing biotic transformations chemically and morphologically. Such characterization emphasis heavily relies upon identifying key or diagnostic bioactive transient or intermediate molecular species in important bioprocesses either supplying or appropriately finishing industrially important materials. Moreover, since both design and in-service performance of modern technological product materials may be subject to environmental alterations invoked by biological agents, our work emphasizes both isolation or production, as well as in-service durability. Key molecular requirements therefore include uniform establishment of both element- and molecular-specific detection capabilities at functional natural or environmental in-vivo concentrations, typically ranging from parts-per-million to parts-per-trillion for analyte elements.

In-Situ Element- or Molecule-Specific Microimaging of Bioactive Substrates

Reliable application of acceptable on-line biomolecular characterization suited for materials bioprocessing must also avoid uncontrolled inhibition or alteration of the key cellular activities and events delivering desirable and designed biotransformations by either endo- or exo-cellular metabolisms. Consequently, we place strong emphasis upon adapting acceptable non-invasive or non-destructive bioprocess monitoring techniques.

We have successfully constructed and demonstrated applications of both microscopic FTIR and EMI, respectively, for isolation of key metabolic pathways rendering potential industrial mining application of fungal dephosphylation (as orthophosphate bioproduct) of major iron ore supplies (FTIR), and bioextraction or bioaccumulation of strategic or advanced technology metals such as yttrium crucial to emerging superconductor industry or gallium essential to semiconductor production.

Molecular Signatures and Recognition as Bioprocess Predictors

In collaboration with IMSE guest scientists, a complete NIST computer program has been successfully demonstrated with capability to assess energetically likely molecular configurations and van der Waals total surface area for quantitative structure-activity relationships. We have demonstrated that total surface area is a reliable predictor for both physicochemical and biological properties, such as metal solubility, chromatographic partitioning, biouptake, and toxicity.

Exocellular or Respirant Metabolic Bioprocess

In addition to our extensive effort for on-line substrate monitoring and selection of optimal microbiological agents for inorganic materials bioprocessing, we conduct intensive studies on the production of metabolites excreted from cells that can induce or transform available source materials to technologically significant isolated or finished products. Two prominent demonstrations include the application of a globally abundant algal product, methyl iodide, and another gaseous bacterial product, trimethylstannane, issued by a common aerobic estuarine heterotrope isolated from the Chesapeake Bay.

In monitoring these exocellular bioprocesses, we also employ both gas and liquid chromatographic separation schemes significantly enhanced by either coupled atomic absorption or flame photometric detectors, affording direct element-specific molecular characterization. Aqueous flow bioreactors incorporating algal methyl iodide serve as effective solubilizing systems for many metal ores and bulk metals, wherein the key mechanistic path involves oxidative methylation of the metal or metalloid centers. Even with bulk iron, a transient methyl-iron species forms which undergoes rapid protolysis to yield methane (or CH_3D in D_2O) plus ferrous ion. In other bioreactions, we observed similar transient methylmetal production by either the active carbonium ion (from CH_3I) or carbanion (from $(CH_3)_3SnH$). In contrast, for precious metal centers, including gold, platinum, palladium, and rhodium, a reductive demethylation step occurs in presence of halide ions to yield pure microcrystalline metal depositions.

MECHANICAL PERFORMANCE OF POLYMERS

The Mechanical Performance Group provides data, standards and concepts of the mechanical properties of polymers, long term performance, and relationships among structure, properties, performance and processing. Activities center on characterization of mechanical behavior and solid state polymer structure. Augmentation of methods to determine structure by scanning tunneling electron microscopy (STM) has led to increased capabilities to elucidate structural details at the molecular level by direct imaging. Information gained by STM will bridge the gap between the size scales of conventional electron microscopy and spectroscopic techniques. STM has been used in our laboratory to examine graphite fibers as preliminary to the study of polymer structure at or near graphite fibers.

The group continues a strong spectroscopic effort focussed on solid state NMR and infrared spectroscopy. An NMR technique utilizing off-resonance proton decoupling has been developed to delineate spectral features due to methylene and methine carbons. Solid state NMR has also been applied to determinations of the molecular conformation in polymer gels and intimacy of mixing in polymer blends. The US Air Force Wright Patterson Materials laboratory and the US Army Aberdeen Proving Grounds support work aimed at elucidating the structure of polymer blends by NMR.

Mechanical properties and performance characterization and modeling has been carried out on polymer glasses, gels, semi-crystalline polymers, and polymer solutions. Parallel studies of the mechanical response and structure are conducted to better understand structure-properties relationships in polymer gels. Continuum mechanics treatments have focussed on descriptions of the mechanical response of polymers subjected to multiple step deformations. A constitutive relationship has been formulated which accounts for the discrepancies between the observed creep and stress relaxation behavior and that predicted from the BKZ theory.

FY 88 Significant Accomplishments

- The surface morphology of graphite fibers was examined by scanning tunneling microscopy with a lateral resolution of better than 10nm. The surfaces of the fibers was rough, with elongated asperities a few tens of nm wide and a few hundred nm long.

- An off-resonance NMR method was developed which is most useful to resolve methylene and methine resonances in rigid solids. Separation of methine and methylene resonances is important in cases where the chemical structures are not completely known or where resonance assignments are required.

- A constitutive equation has been developed which, for the first time, describes the nonlinear mechanical response in a stress relaxation experiment for a semi-crystalline polymer. The predictions of the new description are in good agreement with data from a series of single and multistep stress-relaxation experiments done in uniaxial extension on an ethylene-hexene copolymer.

Characterization of the Solid State Structure and Morphology

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Projects concerned with characterization of the solid state structure and morphology of polymers focus on crystallizable polymers, polymer blends, and polymers at the surface of graphite fibers. Details of the structure at the molecular level were investigated with spectroscopic techniques and by molecular modeling, while larger structural features were studied by electron microscopy, optical microscopy and scanning tunneling electron microscopy. Details of the single chain structure of isotactic polystyrene (iPS) prepared from physical gels were clarified. Other studies were aimed at elucidating the lamellar growth and proliferation processes which govern the progressive evolution of spherulites from single crystal-like precursors in iPS crystallized from the molten state. An investigation was initiated on polyphenylene sulphide (PPS), which is of interest as a high temperature thermoplastic matrix material of carbon fiber composites. Current work on PPS is described in the Processing and Reliability of Polymer Composites portion of this report.

Model calculations are providing a view of the molecular architecture of chain entanglements which provide the connections between polymer molecules that yield the macroscopic mechanical properties observed in polymeric materials. For example, ultra-high strength fibers of polyethylene are made by spinning a solution of entangled polymer molecules.

Solid state nuclear magnetic resonance (NMR) techniques have been used to ascertain the degree of component mixing in polymer blends at the molecular to tens of nm range.

Morphology of Isotactic Polystyrene

In an previous study, it was shown that during the early stages of evolution of iPS spherulites from the molten state pronounced interlamellar splaying was manifested in the initially formed multilayered precursor crystals. Furthermore, this occurred prior to the development of any distinct degeneration in the lateral growth habit of the lamellar layers from their intrinsic hexagonal habit to an elongated but narrow lath-like ("fibrillar") habit typical of the more advanced stages of formation of spherulites. The question concerning the origins of the above mentioned occurrence of splaying is whether or not it is mainly a consequence of the segregation of low molecular weight and stereo-irregular chains between individual lamellae or stacks of several lamellae. Exploratory experiments on the crystallization of iPS from dilute solutions (e.g. 0.04% solutions of the polymer in 1:2 1-chloronaphthalene/dodecanol solvent mixtures), yielded interesting results in this connection. Segregation effects would be expected to be minimal in crystallization from dilute solutions. Yet, complex rosette-like multilayered crystals in which the constituent lamellae exhibit splaying as well as curved conformations akin to those in the melt-grown precursors of spherulites were grown from dilute solutions. This similarity, revealed by scanning electron microscopy, may be adduced as evidence that the splaying and curvature in the melt-grown spherulite precursors are not mainly induced by segregation effects.

The formation, from dilute polymer solutions, of lamellar crystals which exhibit variously curved conformations has been observed in other polymers. At the root of an understanding of the origins of the curved conformations of lamellae is knowledge of the interrelationships between curvature, the sectored character of the chain-folded layers, and the incidence of screw dislocations from which new layers are initiated. Resolution of these features involves the use of transmission electron microscopy (TEM), with the appendant limitations on sample thickness. The above mentioned rosette-like multilayered structures were too thick for this purpose.

In order to obtain detailed insights into the origins of the formation of curved lamellae of iPS and the manifestation of interlamellar splaying under conditions in which the effects, if any, of "impurity" segregation are minimized we have undertaken a systematic study of the effects of crystallization conditions on the habits of iPS crystals grown from dilute solutions. Our objectives are: (a) To initially establish conditions in which the polymer crystallizes in the form of six-sectored chain-folded monolayered (and hence electron transparent) crystals. (b) To then systematically vary temperature and/or concentration such as to favor more rapid crystallization, which usually leads the formation of multisectored lamellae as well as to the occurrence of a higher incidence of screw dislocations and the proliferation therefrom of additional chain-folded layers. (c) To determine whether any correlations can be established between the conformations (curvatures) of the lamellae formed under different conditions, the extent to which the lamellae are multisectored, the incidence of screw dislocations, and the occurrence of interlamellar splaying. All these goals remain to be achieved. The crystals grown under the conditions of crystallization which have been probed so far have been multilayered. Examination in a scanning electron microscope revealed that, as is the case in the above mentioned rosettes, their constituent lamellae were curved. While differences in interlamellar splaying have been observed, the species of crystals grown so far were, in the most, too thick for examination with a transmission electron microscope. In some rare cases it was possible to examine regions near the edges of crystals in transmission. It was evident from the appearance of the lamellar texture in these regions that the lamellae were multisectored, and that the proliferation of lamellar layers was associated with a high incidence of screw dislocations. Detailed comparisons between the fine structures of the various species of crystals have as yet not been possible. On-going experiments in connection with electron microscopical studies in transmission include attempts to isolate the multilayered crystals from the polymer solutions at earlier stages of growth (and hence of chain-folded layer proliferation) than has been tried so far.

Ordered, Solid-State Forms of Isotactic Polystyrene

In work which grew out of a study of gels of isotactic Polystyrene (iPS) and decalin (cis- or trans), an important consideration was whether the iPS in the solid phase of the gels constituted an ordered phase, e.g. a crystalline phase. In the literature, it was suggested that iPS in the gel state adopted an ordered structure having an 'extended chain' conformation. In fact, a 12_1 helical conformation was ascribed to the iPS chains instead of the usual 3_1 helical conformation found in solution grown crystals of iPS or glassy iPS samples annealed at temperatures above T_g. The evidence for the 12_1 helical structure in the gels usually came from observations on dried gels; so there remained the question whether the original gels exhibited this same structure.

An 'extended chain' crystal structure is also ascribed to samples exposed to certain solvent vapors, e.g. cyclooctane vapor. In this case, the vapor generally produces some 3_1 helical crystals and some extended chain crystals, the mixture depending on the temperature of solvent exposure. By implication, these extended chain crystals are related to the gel-state structure in iPS gels. Since vapor-induced crystals could never be observed in samples completely devoid of the original solvent, and since x-ray data for lateral spacings in these extended chain crystal structures were sensitive to the particular solvent used to produce the ordered structures, it was postulated that there was probably solvent in the lattice of these extended-chain structures.

^{13}C experiments were conducted in order to probe the similarity or dissimilarity between the ordered states of iPS annealed glasses, iPS glasses exposed to cyclooctane vapor, and iPs gels of trans-decalin (both original gels and dried gels). ^{13}C spectra taken with cross-polarization and magic angle spinning (CPMAS spectra) will yield spectra which are sensitive to the packing geometry. Although a given spectrum cannot be interpreted in terms of a unique chain packing, changes in lateral packing can be inferred from shifts in the positions of spectral lines.

Results of this work which is still in progress are as follows:

a) The spectrum of the 3_1 helical crystal has sharper and more numerous lines than any of the other ordered states.

b) The spectrum of the cyclooctane-vapor-induced (CVI) crystals is different from that of the 3_1 helical crystals. Particularly different are the positions of the protonated aromatic carbon resonances. Indications are that the aromatic rings in this structure are flipping by 180 degrees since the linewidth and relaxation times associated with the para carbon are narrower and longer, respectively, than for the ortho and meta carbons on the ring. It is also significant that the unprotonated ring carbon is split into a doublet indicating that this ordered structure has nonequivalent sites within the unit cell associated with that carbon position. It is not at all clear that the proposed crystal structure allows for such nonequivalence. It is likely that the true crystal structure is more complicated than has been proposed. The mobility exhibited by the aromatic rings at ambient temperature implies that the CVI crystal structure is not as densely packed as the 3_1 helical crystals. In this context, the possibility that solvent exists within the crystal lattice must be taken seriously.

c) The spectrum of the ordered structures within a dried gel is more difficult to isolate than was the spectrum of the CVI crystals since 78% of the iPS residues exhibit a glass-like spectrum. Nevertheless, the CPMAS spectrum of the ordered regions of a dried gel, made from a gel of iPS and trans-decalin, showed a spectrum different from either the CVI or the 3_1 helical crystals. In particular, the aliphatic resonances were shifted upfield 1.5 - 2 ppm compared to the other two crystal forms. Again, the protonated aromatic region did not show very much multiplicity implying that there was some motional averaging of the ring resonances occurring.

d) The CPMAS spectrum of a 25%iPS/75%trans-decalin gel gave indication of an ordered structure, more ordered than the glass, yet less ordered than the 3_1 helical crystals. One of the unique features of the gel spectrum was the upfield shift of the aliphatic resonances, compared to the same resonances for the 3_1 helical crystals, the CVI crystals, or the iPS glass. Thus, based primarily on the similarity of the aliphatic resonances in the original gel and the ordered regions of the dried gels, it is postulated that the dried gels carry a memory of the ordered structures present in the original gels. Yet, based on the spectra, this ordered structure is different from that of the CVI or the 3_1 helical crystals. Perhaps a relevant point is that trans-decalin will not promote vapor-induced crystallization.

e) The CVI crystal and the dried gel preparations each had residual solvent which could not be removed by extensive vacuum pumping at ambient temperature. The percentages by weight of solvent in these two preparations were about 15 and 10 respectively. Proton NMR showed that the solvent resonances in these two preparations gave relatively narrow linewidths which, in turn, indicated extensive motional averaging on the microsecond timescale. Therefore, if the solvent is in the ordered phases, it must be quite mobile. An attempt was made to ascertain, via proton spin diffusion (really polarization transfer), whether the solvent was in the CVI lattice. The interpretation of this experiment was ambiguous since the initial polarization transfer occurred about equally strongly to the disordered phase and to the CVI crystal phase. One possibility consistent with experiment is that the cyclooctane exists primarily at the CVI crystal/amorphous interface. Another possibility is that the cyclooctane exists both in the CVI crystalline phase and certain regions of the amorphous phase. A model eliminated by these results is that the solvent is uniformly distributed throughout only the amorphous phase.

Intimacy of Mixing in a Crosslinked Blend of PEG/PMVT

In a continuation of work for the US Army Aberdeen Proving Grounds, we examined the intimacy of mixing of a mixture whose proportions by weight were 0.6:3.0:5.0 of diisocyanate crosslinking agent, IPDI, poly(ethyleneglycol), PEG, having $M_w = 1000$, and poly(methylvinyltetrazole), PMVT. The stoichiometry is chosen so that the IPDI can react to completion with 90% of the hydroxy termini of the PEG to form urethane-type crosslinks. The crosslinking is done following a blending of all of the components. While the low MW PEG seems compatible with the much higher MW PMVT in a blend of these two components (only one T_g is observed), there is a question whether any phase separation occurs as a result of the MW increase of the PEG upon crosslinking. There is also the question whether NMR can detect any specific interaction between the PEG and PMVT chains, e.g. via chemical shift changes.

The NMR work undertaken this year involved taking CPMAS spectra at temperatures below ambient. At temperatures around 240K the molecular motion is mostly frozen out such that only very restricted motions take place. Under these conditions, one can conduct proton spin diffusion measurements via the carbon CPMAS spectra and interpret the results with reasonable confidence from the known diffusion constant. The experiment involved producing a proton polarization gradient between the PEG and PMVT protons and then observing the gradient decay with time as a result of spin diffusion. It was found that we could not produce large polarization gradients; moreover, those that were produced had vanished in 2 ms as a result of spin diffusion. Both of these observations are consistent with intimate mixing in the sense that if the PEG and PMVT tend to phase separate, their minimum domain dimensions have an upper limit of 3 nm. There was no direct spectral evidence for interaction between the PEG and PMVT repeat units.

Chemical Investigation of Thermally Polymerized Monomer Mixtures

We used our newly assembled 2.35T spectrometer to sort, via ^{13}C CPMAS NMR, the chemistry associated with thermal polymerization of a bisbenzocyclobutene (BCB) and a bismaleimide (BMI). These materials were received as part of an Air Force contract. Previous results were based on spectra obtained at 4.7T. The higher field spectra have two characteristics which differ from the lower field spectra. First, at our achievable spinning rates of 4 kHz or less, aromatic sidebands at 4.7T always interfere with the aliphatic centerbands so that the aliphatic resonance profiles cannot be isolated cleanly; at 2.35T this problem does not occur. Second, carbons near to ^{14}N nuclei experience a residual dipolar broadening which, in ppm, scales as B_o^{-2} where B_o is the static magnetic field. Therefore, at 4.7T, compared with 2.35T, the resonances of those carbons bonded to nitrogens (both BMI and BCB possess nitrogens) becomes as much as 4 times sharper. This field dependent broadening yields information not available at a fixed field since the linewidth of a given carbon bonded to such a nitrogen experiences other kinds of broadening also; moreover, the amount of dipolar broadening at a given field is related to the magnitude of the particular electric field gradient at the bonded ^{14}N nucleus. Thus, if a chemical reaction takes place close enough to a nitrogen to change its electric field gradient, taking spectra at two fields will expose this change.

The results obtained previously were confirmed by the spectra at lower field. In particular, the reaction of BCB and BMI does not produce an alternating copolymer of BCB and BMI via a Diels-Alder addition. The new data also showed that:

a) The true aliphatic lineshapes deduced at higher field in the presence of the aromatic sidebands were reasonably accurate.

b) Polymerization of BCB with itself, BMI with itself, or an equimolar mixture of BCB and BMI always resulted in a substantial (the order of two-fold) reduction in the ^{14}N quadrupolar coupling constants. This change is reasonable in the case of the ^{14}N nuclei in BMI since the normal reactive site is in the same five-membered ring as the nitrogen. For BCB, however, the most reactive site is on a six-membered ring singly bonded to the nitrogen on an adjoining five-membered ring. It is not expected that a chemical reaction at a site so remote from the nitrogen should influence its quadrupolar interaction so dramatically. Thus, the data suggest that ring-opening is occurring on the five-membered ring containing the nitrogen. It is also clear from other resonances that the cyclobutene ring, the primary site of expected reaction, is indeed reacting to near-completion. Thus, while the chemistry is not completely elucidated, it becomes clearer that BCB is undergoing some very complex chemical reactions and that the products result from multiple, competing pathways.

c) In BCB and equimolar mixtures of BCB and BMI the aliphatic carbon intensity, relative to the total intensity, grows at a rate faster than expected upon polymerization. This observation suggests that BCB is undergoing more reactions than just the opening of the cyclobutene ring followed by addition across a double bond. In fact, an increase in the fraction of aliphatic carbons may suggest a reaction of double bonds with one another, as in the polymerization of alkenes.

Modeling of Entanglements Embedded in Polyethylene

Ultra-high strength fibers of polyethylene are made by spinning a solution of entangled polyethylene molecules. The entanglements are incorporated into the fiber, which may be highly crystalline. Models of entanglements which are suitable as starting points for calculation of minimum energy conformations were made. Rules similar to those that define crystallographic defects were applied to create primitive entanglements that are completely embedded in a polyethylene crystal. The entangled chains all approach their proper lattice sites as they are followed away from the entanglement region. The most primitive entanglements are linked, U-shaped chains with the stems that form the "sides" of each U on adjacent rows of crystallographic sites. An example is two linked chains with the two stems of one U running in one direction in a (110) plane with the two stems of the other entangled chain running in the opposite direction in an intersecting (110) type plane. The chain stems in this entanglement, plus the chains in two surrounding shells involve a total of 24 stems. The distortions of chains beyond the second shell appear to be small. A model of this size can be adjusted to its minimum energy conformation in a straightforward way with computers and software now available. A small family of such primitive entanglements was defined. Such entanglement models provide a basis for examination of the interactions between entanglements and other crystallographic defects such as dispirations and dislocations which may allow a chain to slide through the entanglement to produce the slow creep which limits some applications of gel spun high strength fibers.

Scanning Tunneling Microscopy of Polymer Molecules and Carbon Fibers

Graphite fibers seven microns in diameter were positioned under the tip of a scanning tunneling microscope, using a specially constructed moveable stage and related apparatus. The surface morphology of the graphite fibers (AS4) was examined with a lateral resolution of better than 10 nm. The surfaces of the graphite were rough, with elongated asperities a few tens of nm wide and a few hundred nm long. The scanning tunneling microscope provides an incisive method for characterization of the surface morphology both at this scale and at the atomic scale.

A review of progress in scanning tunneling microscopy applied to molecules and carbon fibers was written. Reports of observations of DNA, small organic molecules attached to carbon or metal surfaces, and changes in the shape (and therefore the chemical structure) of small molecules resulting from the application of a voltage pulse through the tunneling tip have appeared. Polyoctadecylacrylate molecules were observed at the atomic scale on graphite and other substrates. Parallel fibrils as small as 0.8 nm and triangular structures consistent in scale with the side branches were observed. Voltage pulses applied to the scanning tip modified and apparently cut through the fibrils.

These sorts of observations which are beginning to appear in the literature provide a basis for expecting to see the behavior of single polymer molecules on the surface of a graphite fiber with the scanning tunneling microscope. Such a capability would provide new information about the interactions between the reinforcing fiber in an advanced composite and the matrix molecules, or other molecules added to improve the behavior of the interface region.

A manuscript entitled "Morphology of Polymer Films and Single Molecules" which summarizes our work on the use of the transmission electron microscope to develop procedures for preparing polymer samples suitable for examination at the molecular scale was prepared. A variety of methods used to prepare dispersed single molecules and very thin films, some of which had network-like regions with fibrils containing only a few molecules, are summarized. Staining with RuO_4 proved be a generally applicable way to observe structures at the surface of a thin film on the scale of the molecular diameter. Structures observed for different polymers were reproducible and characteristic of each polymer.

Measurement and Modeling of Mechanical Properties and Performance

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Reference Standard Polyethylene Resins and Piping Materials

Polyethylene currently accounts for approximately 80% of new natural gas distribution piping in the United States. The Gas Research Institute has sponsored a program at NIST to provide reference materials for use in research related to natural gas distribution systems. This program has included the procurement, characterization, and issuance of reference materials of a pigmented and unpigmented pipe resin as well as piping and joints manufactured from the pigmented resin. During the past year, work focussed on the characterization of the melt flow rate properties and mechanical behavior of material taken from the two types of T-joints for which preliminary work had indicated a significant difference existed between the melt flow rates. The melt flow rate has now been redetermined for material taken from several locations within five different joints of each type. It was found that the melt flow rate data for the two types of joints differ significantly from one another and also differ from that of the resin. One of the purposes of our more recent work has been to determine whether the changes in melt flow rate caused by the processing are accompanied by changes in the mechanical behavior. Such changes may have relevance with respect to long term performance. Two aspects of the mechanical behavior were examined. The environmental stress-crack resistance (ESCR) of material taken from both types of joints and the starting resin was determined using a test method developed in our own laboratory. The tests were carried out at 75°C using an applied load of 5 MPa and in the presence of a stress-cracking liquid. The increase in melt flow rate observed for the butt fusion joint is accompanied by a decrease in ESCR, whereas the decrease in melt flow rate found for the socket joint is accompanied by an increased in ESCR.

Uniaxial creep experiments were also conducted on material remolded from the two joints and the resin. In the region of largest strain, after the thinned down portion of the specimen has propagated the entire gage length of the specimen (necked and drawn material), the creep curves plateau at which point there is nearly a complete cessation of creep. In this region, the stretch ratio λ can vary from about 6 to 9 depending upon the level of applied stress. For the specimens under the three highest loads it was found that the strain in the plateau region is consistently slightly higher in the material from the butt fusion joint than in that from the socket joint. This trend is consistent with the behavior observed in other polyethylenes where it is found that the higher the molecular weight is the less the maximum stretch is that can be achieved under a given load prior to failure.

A more striking difference in behavior occurs for the three specimens under an applied stress of 10 MPa. Up to a time of about 10^3 minutes all three materials, including the specimen molded from the resin, show essentially the same behavior. However, beyond 10^3 minutes the creep of the material from the socket joint departs significantly in behavior from the other two. For example, at the time at which the specimens from the butt fusion joint and the resin exhibited neck formation ($\approx$ 60% strain) the material from the socket joint has only attained about one half the value of strain. The two specimens under an applied stress of 9 MPa also appear to be showing the same differences. However in this case several years may be required before the difference in creep strain becomes comparable to the specimens at 10 MPa.

The results just cited indicate that the changes in melt flow rate brought about by the processing are accompanied by measurable differences in the long term mechanical behavior. The results suggest that in the socket joint sufficient crosslinking and/or long chain branching occurred during the processing to result in an apparent increase in the molecular weight and/or molecular weight distribution. On the other hand, in the butt fusion joint some slight amount of degradation may have occurred. It remains to be determined to what extent these changes may affect long term performance under normal use conditions. One phenomenon of concern to the gas industry is that of slow crack growth in piping materials. The differences observed here may well have relevance to this process. Further work is needed to better define and understand the molecular and/or morphological changes taking place which involve very long relaxation times, and the way in which these processes may lead to instabilities such as those that lead to neck formation or stress-crack failure.

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

For crystallizable polymers such as polyethylene it is found that the mechanical response in a stress relaxation experiment, even at quite small deformations, is nonlinear and cannot be described quantitatively by the BKZ theory. A better description of the behavior has been obtained using a new constitutive equation proposed by Zapas. The predictions of both the BKZ theory and the new description are shown for a series of single and multistep stress-relaxation experiments done in uniaxial extension on an ethylene-hexene copolymer of the type used in natural gas distribution piping. The results of the calculations using the new description are encouraging and are in good agreement with experiment. Also examined was a strain history involving a constant rate of strain experiment in which the strain was cycled up and down, and a considerable degree of success was achieved in describing the observed behavior using the same equation. To our knowledge this represents the first time that a description of this particular type of strain history has been successfully given for a nonlinear viscoelastic material. It appears that the new formulation provides the necessary ingredients to describe quantitatively the observed behavior.

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

In a single step stress-relaxation experiment, a finite time is required to apply the step in strain. As a result, some uncertainty is introduced into the observed behavior at the early times during the experiment. Several years ago an approximation was derived which can be applied to shear stress-relaxation experiments when the deformations are small and the stress-strain behavior is linear. We have extended this idea and have derived some approximate relations which can be applied to measurements made in simple extension in the region where the behavior is nonlinear. The derivation is based on the assumption that, for the particular types of strain histories under consideration, the BKZ theory can be used as a one dimensional description. In the new formulation the stress $\sigma(\epsilon,t)$ at any time t after a step in strain ϵ is given by

$$\sigma(\epsilon,t) = K(\epsilon,t-t_1/2)\, A(\epsilon,t-t_1/2) \qquad (1)$$

$K(\epsilon,t-t_1/2)$ is the value of the stress-relaxation function at any time t after a step in strain ϵ, and t_1 is the time required to apply the step in strain. $A(\epsilon,t-t_1/2)$ is a correction term given by

$$A(\epsilon,t-t_1/2) = \frac{2C}{1+\epsilon/2}\left[1-\frac{K\left(\frac{1+\epsilon}{1+\epsilon/2},t-t_1/2\right)}{K\,(1+\epsilon,t-t_1/2)}\right] \qquad (2)$$

where C is a constant. In order to calculate $A(\epsilon,t-t_1/2)$it is necessary to determine $K(\epsilon,t-t_1/2)$ at two different levels of strain, namely ϵ and $\epsilon/2$. As the step in strain becomes smaller and smaller and the ratio t/t_1 becomes larger $A(\epsilon,t-t_1/2)$ approaches unity and equation (1) becomes equivalent to the original approximation.

In order to demonstrate the validity and usefulness of the approximate relations, we have obtained data on an ethylene-hexene copolymer at 26°C. A series of single step stress-relaxation experiments was done in which the strain during the stress-relaxation portion of the experiment was 0.3%, 3%, and 6%, and the step time t_1 was varied from 0.1 s to as long as 100 s. For this type of crystalline polymer it is found that the slope of the stress-relaxation curve, when plotted on log-log paper, is linear and independent of the strain. In this event the theory shows that only one experiment is needed in order to obtain a good approximation to the nonlinear surface describing the single step stress-relaxation behavior and the function $K(\lambda,t)$ can be represented by the relation

$$K(\lambda,t) = \phi(\lambda)t^{-\alpha} \quad . \qquad (3)$$

By determining $A(\epsilon,t-t_1/2)$ for different values of ϵ and the ratio t/t_1 we were able to correct the early time data to bring them into agreement with the curves obtained from the experiments involving the shortest step time. The procedures outlined should be particularly useful in instances where it may be desirable to reach the predetermined strain via a slower ramp function, the purpose being to avoid possible rapid heating or even fracture of the specimen during application of the step in strain.

A Phenomenological Theory of the Influence of Strain History on the Rate of isothermal Stress Relaxation

Constitutive relations were formulated for a class of incompressible viscoelastic fluids for which internal structural changes occur at a rate that is influenced by the history of the strain. For the materials considered, the contribution to the stress at time t made by the strain at an earlier time τ is a function of that strain, the true elapsed time $t-\tau$, and a quantity $\Theta(t,\tau)$ that can be interpreted as the elapsed time measured by a clock whose rate of advance, because it is tied to the rate of structural change, is affected by the history of the strain. The functional relating $\partial\Theta(t,\tau)/\partial t$ to the history of the strain up to time t is assumed to have the same domain and a structure similar to that relating stress to strain history. The present theory reduces to the theory of BKZ fluids in the (extreme) special case in which $\Theta(t,\tau) \equiv t-\tau$, i.e., in which $\partial\Theta(t,\tau)/\partial t \equiv 1$. It was shown that a constitutive relation recently found to account well for observed discrepancies between experimental observations and predictions of the BKZ theory can be considered first-order approximation to the relations formulated.

Consider a body B in motion, and let $\xi_\alpha(x,\beta)$ be the place in space at time β of the material point P that is at x at time α. The value at P of the gradient of the deformation taking the configuration at time α into the configuration at time β is

$$F_\alpha(\beta)=\mathrm{grad}_x \xi_\alpha(x,\beta)$$

This invertible tensor $F_\alpha(\beta)$ is called the deformation gradient (for P) at time β relative to time α. For the same material point, the left Cauchy-Green tensor $B_\alpha(\beta)$ (at time β relative to time α) is the positive-definite symmetric tensor given by

$$B_\alpha(\beta)=F_\alpha(\beta)F_\alpha(\beta)^T$$

Making assumptions about the form of the quantity $\Theta(t,\tau)$ which are consistent with the principle of material indifference we obtained the following equation

$$S_D(t)=\int_{-\infty}^{t}\Psi(B_\tau(t),\ t-\tau)d\tau + \int_{-\infty}^{t}\Phi(B_\tau(t),t-\tau)\int_{\tau}^{t}\int_{-\infty}^{\zeta}\phi(B_\nu(\zeta),\zeta-\nu)d\nu\ d\zeta\ d\tau + O(\epsilon^2) \qquad (1)$$

where $S_D(t)$ is the stress deviator.

With this equation we were able to describe two step stress relaxation experiments in concentrated solutions of polyisobutylene and polystyrene in ranges in which departures from the BKZ theory are large. An analysis, to be published, of data recently obtained by Crissman and Zapas for multistep, low strain, motions of bars of high-density polyethylene indicates that the behavior in elongation of semicrystalline polymers also can be described by Eq. (1) in circumstances in which the BKZ theory does not hold.

The Free Energy Function of Crosslinked Rubbers

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

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

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

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

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

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

The experiments carried out in this task include mechanical and swelling tests on dicumyl peroxide crosslinked natural rubber. We have crosslinked the rubbers with from 0.6 to 20 parts per hundred peroxide. Torsion experiments are carried out in which the torque and normal force are measured as functions of time and deformation. From these results the value of $\partial\Delta A/\partial\lambda$ in equation 1 can be calculated. Swelling has been carried out for each of the crosslink density rubbers in a series of six solvents including good, poor and non-solvent systems. The swelling results are used in the calculation of the mixing free energy term in equation 1.

In future work we will measure the elastic free energy derivative of the rubbers in the swollen state and compare it with that determined from the dry state measurements. In addition, experiments to examine the possibility that equation 2 is a universal function in terms of some critical crosslink density, υ^*, are being designed.

Relaxation of Crosslinked Networks: Theoretical Models and Apparent Power Law Behavior

There have been several reports recently in which molecular models were proposed to account for the relaxation behavior of crosslinked networks. All of the models have been based upon the assumption that the long time relaxation in networks is due to "dangling" chains that are attached to the network at only one end. Importantly these theories predict that the relaxation of the network in the terminal zone follows a power law in time, but differ in their predictions of the power law exponent.

On the other hand, the experimental data generally cited in support of a power law relaxation are taken from studies by Chasset and Thirion on dicumyl peroxide crosslinked natural rubber. These data and other data by Plazek do not support a power law relaxation function for crosslinked rubber.

We have reviewed the theories and the data relevant to the question of the relaxation of network polymers. The data of Chasset and Thirion were reanalyzed and it is shown that, while power law behavior is observed over a limited time range, the general behavior of networks is not well described by a power law relaxation function. Rather, the important phenomenon of relaxation in networks is the existence of a time-crosslink density superposition principle. This is an experimental observation which cannot be explained by the current theories of relaxation in networks.

Analysis of the Effects of Instrument Compliance on the Transient Normal Force Response in Cone and Plate Viscometers

An analysis and series of experiments were performed to better understand the transient normal force response in shearing experiments in the cone and plate geometry. In our analysis we considered the response in single step stress relaxation experiments. Results from experiments on a polyisobutylene solution show deviations from unity of the ratio of the first normal stress difference to the product of the shear stress times the shear strain. This ratio, which we refer to here as U, is less than unity at short times and increases to values greater than unity, possibly decreasing back towards unity at long times. The so-called universal value of U is 1 from continuum mechanics.

The deviations of the response from the theoretical value can be accounted for by including three important corrections in the analysis. First, the analysis shows that the finite time required to apply the step introduces errors in the normal stresses which are greater than those in the shear stress. This effect would result in an apparent deviation from unity in the value of U even were a machine of infinite stiffness used for the experiments. Second, the machine compliance introduces errors in the normal force response by causing an increased gap separation which subsequently relaxes as the normal force relaxes. Third, the constrained geometry of the cone and plate results in the compliance errors being "magnified" by some 1600 times, leading to the need for large corrections and apparent violations of the universal relation at long times.

Experiments were carried out in tension and compression in a parrallel plate geometry to demonstrate this effect in a viscoelastic fluid. It was found that the variation in the magnification effect in this case is similar to that observed in elastic bodies. This is the first time that such results were demonstrated for a fluid body.

Dilatometry of Polymeric Glasses Subjected to Torsional Deformations

Work is continuing in the construction of a torsional dilatometer to be used in the study of three important areas. First, measurements of the volume change of solid polymers in torsional deformations will allow the determination of the W_1, W_2, and W_3 for the first time.(The $W_i = \partial W/\partial I_i$, where the I_i's are the invariants of the deformation tensor and W is the strain energy density function). Such measurements are important in the understanding of the properties of solid polymers at large deformations.

Second, it is known that the volume of a glass changes spontaneously after a quench from above its T_g to below it. The accompanying changes in mechanical properties have come to be known as physical aging. In addition, it is observed that the rate of physical aging is affected by the magnitude of the applied stress or deformation. The resulting "rejuvenation", its interpretation, and the mechanisms underlying it are quite controversial. An important parameter in the controversy is the magnitude of the volume change which would accompany the rejuvenation. In torsion the volume change due to the deformation itself is of second order (vs first order in extension or compression). Then the measurements of volume change in controlled thermal and torsional histories will permit the separation of the volume changes due to the mechanics, the temperature and its history(aging) and any coupling between the mechanical stimulus and the "free" volume of the glass. Such experiments will improve our understanding of the glassy state and its response to mechanical stimuli.

Third, the effects of deformation on the glass transition are controversial. Free volume models would predict virtually no change in T_g upon application of a torsional deformation, whereas the Gibbs-DiMarzio model predicts a measurable increase. We anticipate using the torsional dilatometer to test these predictions.

The dilatometer itself has reached a stage of development where preliminary calibration measurements have commenced. Minor problems have developed and these are currently being corrected in the shops division.

Predicting the Lifetime of Polyester Based Recording Media

An environmental aging study with the purpose of establishing the lifetimes of magnetic tape, of the poly(ethylene terephthalate) base in photographic and electrographic film, and of videotapes has been sponsored at NIST by the National Archives. This project is now complete and the Final Report is in preparation. The approach taken to estimate tape lifetime was to write digital data on tapes, age them at specified temperatures and relative humidities, read the data on the tape after aging, and alternate aging and reading attempts until the tape became unreadable. The goal is to establish lifetime trends which can be extrapolated to estimate a value under typical storage conditions.

Test methods were also developed to monitor tape status during storage. These included: (1) the force required to peel binder from the support; (2) the elongation of the tape at which the binder separated from the support; (3) the number of rolling translations of a crease required to separate the binder from the support; (4) the water content of the tape at 45% relative humidity; and (4) the change in weight of the tape during aging. It was found that all five quantities changed significantly after aging, but did not consistently correlate with tape lifetime, tape lifetime being defined as the ability to read the digital data stored on the tape.

The aging results for PET indicate that the material should be quite stable at ambient conditions provided that the process by which PET is made and the rather specific combination of orientation and crystallinity now given the polymer are not changed substantially. The combination of high temperature and high relative humidity can cause rapid deterioration of the integrity of the film base. The principal mechanism of degradation is hydrolysis. As few as one chain scission per molecule is sufficient to cause serious loss in physical properties.

Both coated and uncoated electrographic film lost tensile strength and elongation to binder separation faster than did the PET film base. This observation might be used to advantage in the storage of magnetic tapes. Films of this type, if stored under the same conditions along with archival materials, should provide an early indication of impending failure.

Comparisons between the characteristics of video and magnetic computer tapes at 23°C revealed significant differences. The average peel force and elongation for binder separation were 0.43 Newtons and 47% for the unaged video tapes, whereas for the unaged computer tapes they were 2.6 Newtons and 108%.

Video tapes aged at 60°C and 75% RH showed a decrease in peel force and elongation for binder separation of approximately 50% after 370 days of aging, whereas the computer tapes, on average lost a much higher percentage of their initial values after an even shorter aging period at 35°C. The video tapes showed only small decreases in peel force and elongation for binder separation at 30% RH after 564 days of aging and about a 25% decrease in these quantities at 75% RH. On the other hand, the computer tapes experienced larger decreases in both quantities at both levels of relative humidity.

Rubber Standard Reference Materials

The Polymers Division maintains a series of Rubber and Rubber Compounding ingredients as Standard Reference Materials(SRM). These materials are used widely by industry through ASTM standard test methods which specify the NIST SRM's. During the past year the program was maintained through interactions with industrial users--normally testing of samples which the users identified as defective, but which upon NIST retesting were within the original specifications of the SRM. This interaction generally leads the industrial users to reverify procedures of testing and equipment calibration. In addition, SRM 384b (N-tertiary-butyl-2-benzthiazyl sulfenamide) was certified as a rubber accelerator, thus renewing the stock of this material.

POLYMER COMPOSITES

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

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

The initial focus of this expansion will be processing since advances in processing science and implementation of on-line process control are the keys to more rapid and reliable processing. In addition, current NIST programs on the characterization of microstructure in composites will be strengthened to compliment the processing studies. The final step in the program expansion will be in the study of properties and performance. The emphasis will be on establishing the processing-structure-property relationships that are needed to improve our ability to understand and predict performance.

The following sections of this report describe the progress made toward these goals during the last year. The efforts are grouped into three subtask areas: Processing, Structure, and Performance. In the area of Processing, the groundwork has been laid for the development of a processing facility. To obtain industries' advice for this facility, a Workshop was held and 23 companies were represented. Efforts are underway to implement the two processing methods that this workshop concluded were most important for the future. A closer tie to the automobile industry has been established by investigating resin systems with greater potential in that industry. Finally, an other agency sponsored program has developed new, rapid-curing vehicles for printing inks. The technology involved has relevance to the composites field because many applications, such as composite repair, adhesive bonding, and high speed composite fabrication, require materials with rapid and controlled cure.

The second subtask area 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 of crosslinked systems) are of interest. During the past year the work on multiphase toughened systems has continued and new programs on partially crystalline thermoplastics and molecular composites have been added. In addition, a project to investigate the role of precursor structure in the processing and performance of gel spun fibers has been initiated.

The third subtask focuses on the determination of performance properties of composites and their constituents. Projects have addressed the failure behavior of the resin (physical aging effects on fracture), the fiber (compressive strength), and the composites (laminate compression failure). In addition, a new test method for determining a resin's resistance to interlaminar fracture is under development. All of these projects relate to delamination which is a major failure mode for laminated composites. Finally, an other agency program is addressing data base development for composite materials.

To assist in these efforts, the Group utilized cooperative programs and guest experts. The Institute wide Colloquium Series on Composite Materials brought many world renowned scientists to NIST for discussions. Cooperative efforts involved programs with the Departments of Treasury and Defense, and the industrial research laboratory of Interez. Joint programs with Dr. A. J. Kinloch at Imperial College (London), Dr. S. S. Wang at University of Illinois, and Dr. John Gilmer of the University of Pennsylvania continue while new programs with Dr. J. K. Stille of Colorado State University and Drs. Ron Eby and Herzl Chai at Johns Hopkins have been initiated. As part of the last mentioned program Dr. Herzl Chai is spending a substantial part of his time at NBS. A research effort with the University of Massachusetts, Polaroid Corp., and Kyoto Institute of Technology has been developed. Finally, Dr. Andre Lee, a former postdoc at NIST, has joined the permanent staff, and Mr. Chung-Chien Yu from Chun-Shan Institute of Science and Technology in Taiwan has worked at NBS for the last 9 months as a guest scientist.

FY88 Significant Accomplishments

- An industry workshop on polymer composite processing was held at NIST, and more than twenty companies were represented. Attendees included users, manufacturers, and suppliers of composites in the automotive, electronics, aerospace, and other industries. The workshop identified the generic processing methods that will be of most interest to industry in the future and the scientific and technical barriers that hinder the implementation and effective use of these methods.

- A Small angle scattering (SAS) technique was applied successfully to characterize molecular composites. By combining the neutron and x-ray results, the scattering from voids, which in the past has made SAS results difficult to analyze, can now be extracted. The first molecular composite studied was a polyquinoline system, and the results indicated that the rigid rod molecules are not dispersed at the molecular level.

- By varying the processing parameters, the molecular structure and toughness of a model epoxy system were modified. For a given composition, the toughness was found to correlate with the compositional fluctuation measured by small angle x-ray scattering (SAXS). These compositional fluctuations can be controlled by changing the processing parameters so that optimum toughness in the single phase region can be obtained.

- A new technique to measure the resistance of polymer resins to interlaminar crack growth in their composite was developed. This test uses a thin adhesive bond between metal adherents to simulate the constraint on the resin deformation produced in the composite by the fibers. Preliminary results show an excellent correlation between fracture energies obtained in the adhesive joint test and experiments using composites. The new method has the advantages of easy fabrication, small quantities of resin required, and no fiber bridging problems.

Processing

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The Processing subtask included activities in three areas. The primary effort focused on the preparation and implementation of plans for a composites processing facility at NIST and the identification of the most critical scientific and technical questions to be addressed with this facility. In addition, projects were conducted to extend cure monitoring studies to a resin system of interest to the automotive industry and to develop new ink vehicles for air-drying and electron beam curing.

Industry Processing Workshop and the NIST Processing Facility

Composites rank near the top of the list of emerging technologies that are vital to the international competitiveness of U.S. industries. Manufacturing plays a critical role in the cost and reliability of these materials largely because we lack the scientific understanding needed to improve efficiency and implement on-line process control. The expertise and measurement capability developed in the NIST Processing Task form the basis for an expanded program to address these questions. A major step in this process is the construction of a processing facility with at least two different fabrication methods represented. This facility will then be used to: (1) study processing in a realistic environment, (2) implement process monitoring techniques on-line, (3) evaluate processing models, and (4) investigate on-line process control. The facility will also be used to fabricate well controlled and characterized samples for the Structure and Performance Subtasks in the program.

Industry Workshop on Polymer Composites Processing

In developing this processing facility, industry input is critical to help identify both the most important processing methods and the scientific and technical barriers that the facility should be designed to address. In an effort to get this input, an industry workshop on composite processing was held at NIST on October 7, 1987. Through presentations by representatives of major industrial sectors, a series of questionnaires, and discussion aimed at achieving a consensus, the attendees ranked the most promising processing methods and the most important scientific and technical barriers to effective utilization of these methods. The time frame of interest was between 5 and 15 years from now.

The attendees represented 23 different companies including composite users, suppliers, and fabricators. The industries included aerospace, automotive, and electronics. The Workshop represented a highly diversified group with a relatively balanced range of interests. In addition, comments were supplied by a number of industrial people who could not attend, but expressed great interest in the workshop.

The list of most promising processing methods included five techniques, two of which were rated significantly higher than the rest: pressure molding and transfer molding. Pressure molding includes both compression molding and autoclave processing while transfer molding includes both reactive and non-reactive materials. The three remaining processing methods were given roughly equal ranking; they are thermoforming, filament winding, and pultrusion. A major common feature for all five techniques is their potential for development into rapid, cost effective production methods.

In addition to the five selected processing techniques, two technologies that complement processing were also identified as very important. The first is alternative sources of energy input to initiate or facilitate processing, e.g. microwave, dielectric and ultrasonic sources or lasers. The other important technology is the preparation of the resin-fiber starting materials, e.g. powder processing for prepreg, commingled fibers, and resin coated fibers.

The workshop concluded that the most critical scientific and technical barriers are deficiencies in our understanding of the chemical and physical changes that occur during processing. Six areas were identified where the lack of knowledge is most critical. The highest rated problem is the need to understand and control resin flow and fiber orientation during processing. The second area is modeling and control of temperature and heat flow. The concerns here ranged from temperature levels and gradients during processing to the use of alternative sources of energy input. Fiber-matrix adhesion is the third most important area, while data validation, data base development, and standardized tests ranked fourth. The control of morphology, such as crystallinity and phase separation in two phase toughened systems, during processing was listed next. Control of finish and dimensional tolerances is the final area identified, which is of particular concern to the automotive and electronics industries.

In addition, the Workshop suggests that three classes of materials offer significant potential for the future and should be watched closely: thermoplastics, liquid crystal polymers, and molecular composites. The first category is already included in much of the discussion above. The second and third, however, are newer and other problems may emerge.

Plans for the NIST Processing Facility

Based on the results of this workshop and input from other sources, two processing methods were selected for implementation in the first phase of the program: autoclave molding and transfer molding. This means the two techniques rated most highly by the workshop will be covered. The implementation of these techniques is well underway and completion is expected within the next year. The equipment is being designed with two considerations: (1) to maximize the opportunities for on-line monitoring so the processing events can be studied to gain a better understanding of the underlying science, and (2) to facilitate the investigation and implementation of on-line process control. In this way, the most important technical barriers identified by the workshop can be addressed. In addition to these two processing methods, several other techniques are under consideration as possible additions to the NIST processing facility.

Curing Monitoring Applied to Automotive Resins

For a number of years NIST has had an active program to develop, maintain, and correlate a wide variety of cure monitoring techniques. This program takes advantage of NIST's capability in measurement science. There are currently ten different process monitoring methods available in the program, 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, and ultrasonic shear wave measurements), 2) thermal properties (differential scanning calorimetry, DSC), 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 and the associated research were described in detail in last year's annual report.

During the past year, this capability was applied to study a vinyl ester resin (VER) system of considerable interest to the automotive industry because of its fast cure at relatively low temperatures and its reasonable cost. This system involved a resin mixture composed of styrene and a vinyl ester resin with propenoic esters on DGEBA backbone. A peroxide initiator at 1 part per hundred parts of resin was used to cure the resin mixture. One factor hindering the use of such resin systems is the lack of detailed information on cure kinetics and practical data for cure behavior in realistic processing environments.

To address the question of cure kinetics, extensive DSC studies were performed at a variety of cure temperatures. It was found that the VER system reached more than 90% of full cure, even at temperatures as low as 60°C. The T_g, however, was a strong function of cure temperature. By post-curing in the temperature region of 120-150°C, a material with T_g around 113°C was always obtained.

The DSC uses very small samples, and consequently, to investigate cure in a more realistic geometry, both ultrasonic and dielectric measurements were used to study samples cured at 90°C. With both techniques the observed cure rates were much higher than for the corresponding DSC tests. In the ultrasonic test, for example, the majority of the reaction occurred within one minute after a short heat up period. One proposed explanation for this was that the inherently low thermal conductivity of the resin prevented the heat generated internally by the reactions from escaping fast enough to prevent overheating in the center of the sample. The test specimens were 2 to 4 mm thick and 2 cm or more long and wide. This overheating would cause a further acceleration of the reactions producing more heat and perhaps a thermal runaway. To examine this possibility thermocouples were placed in the dielectric and ultrasonic samples. The results indicated that the internal temperatures reached values 30 to 40°C above the control temperature of 90°C. By contrast, the DSC samples are small (~10 mg) and were cured in a sample container with a high thermal conductivity. As a result, this effect was not present and estimates of temperature overshoot were less than 2°C.

Both the ultrasonic and dielectric techniques have the potential for use in realistic, even on-line, environments. The importance of this was observed in the VER studies since sample size was a critical factor. In a practical situation such a thermal run could be beneficial since it reduces the cure time. Modelling and characterization data such as that obtained here would be essential, however, to prevent the internal temperatures from reaching the point where thermal decomposition could occur. Future work will investigate the effects of inert fillers, some of which will certainly change the thermal conductivity. The sample size will clearly be a concern here as well.

Design and Synthesis of Intaglio Ink Resins

In another project NIST is developing new, rapidly curing material systems as ink vehicles for intaglio printing processes at the Bureau of Engraving and Printing. The objective is to achieve better control of the cure rate in air-drying systems and in materials that can be cured with an electron beam. The air-dry systems being developed are based on drying oil technology while the electron beam curing materials use a free radical mechanism.

The performance requirements for the resins impose severe constraints. The viscosity must be in the region of 100 to 500 poises, and the formulated inks, containing the resins and pigments and other solids, must disperse in 1% aqueous sodium hydroxide to which 1% w/w of surfactant has been added. In addition, the resins must keep the various solid ingredients of the inks in suspension.

The series of air-dry intaglio ink resins is based on molecules which are similar to large drying oil molecules. A few alkyds have been included. The drying oil-like molecules, based on polyhydric alcohols esterified with linseed oil fatty acids, have satisfactory viscosity and cure. Dispersion in the alkaline medium used to clean the printing press is highly dependent on the formulation of the ink and on the acid number of the resins. A range of acid numbers is being explored to provide resins with acceptable performance.

The series of resins which cure in electron beams is based on methacrylate groups, which combine readily with the free radicals formed during exposure to the electron beam. Methacrylates have been used rather than the faster-curing acrylates to reduce the toxicity of the resin. An intaglio ink resin is required to be a liquid. However, many methacrylates are solids. Also, the resin has to contain enough methacrylates to cure rapidly and should have as high a molecular weight as feasible. Reactions of a methacrylate-containing alcohol with various acid anhydrides give esters with one free acid group for each ester group. Di-anhydrides give more than one isomer, which tends to make the resultant resin liquid. These materials have more than enough acidity to easily disperse the pigments and other solids in the ink and to disperse well in the alkaline washing medium. Unfortunately, they are so viscous that they must be diluted before they can be used as intaglio ink resins. Fortunately, suitable water-dispersible, very low- viscosity, electron-beam active oligomers are commercially available. Larger quantities of trial air-dry and electron-beam resins are being prepared for tests of toxicity, formulation, and printing.

Structure

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The determination of molecular structure in thermoset resins is the major thrust in the structure subtask of the composite research program. Both neutron and x-ray scattering techniques were applied to investigate the structure of resins based on di-functional and tetra-functional epoxies. The processing-structure-properties relation of these resins has been explored. In addition, research efforts have been extended to include both molecular composites and a high strength/high modulus fiber forming material. Work has also been initiated to study crystallization in partially crystalline thermoplastics since these materials offer significant promise.

Processing-Structure-Properties Relation in Epoxies

One of the common schemes to enhance the toughness of epoxies is to increase the molecular weight of the curing agents in order to decrease the crosslink density. Unfortunately, the glass transition temperatures (T_g) of the epoxy, hence the use temperature of its composites may also be lower. It is desirable therefore to keep the amount of high molecular weight curing agent to a minimum while maintaining as much toughness as possible. Towards this goal, we explored the possibility of enhancing the toughness by optimizing the processing conditions for a given epoxy composition. The basic conjecture pursued in this work is that the toughness of an epoxy formulation can be improved by increasing compositional fluctuation on a micro scale. Based on this conjecture, we modified the processing conditions to enhance the compositional fluctuation. The structure of the epoxies cured under different processing conditions was monitored with small angle x-ray scattering (SAXS).

Diglycidyl ether of bisphenol A (DGEBA) was the epoxy monomer used and Jeffamine* D-230 was the curing agent. A high molecular weight version of D-230 namely D-2000 was the toughness modifier. Both Jeffamines are linear di-amine linked by polypropylene oxide chain. The molecular weight of these two amines are 230 and 2000 respectively as designated in their names. The formulation used throughout this work was 1:20:42 in mole ratio of D-2000:D-230:DGEBA. To change the distribution of the D-2000 di-amine from being homogeneous to partially segregated, we adopted the following processing scheme. The D-2000 di-amine (1 mol) was partially cured with DGEBA (2 mol) in the first stage, followed by mixing with the rest of DGEBA and D-230. The final mixture was then fully cured at 100°C for 24 hrs. It was found that eight hours at 100°C was needed for the D-2000 (1)/DGEBA (2) to reach gelation. Accordingly, the precure time for D-2000 and DGEBA was varied from 0 to 6 hours. The toughness was measured with precracked compact tensile test. T_g was measured with DSC. Scattering invariance (I_{SAXS}), an indictor for the extent of compositional fluctuation, was calculated from SAXS data. The results are listed as follows:

Processing-Structure-Properties of Epoxies

Precure time (hrs)	Fracture Toughness ($MN/m^{3/2}$)	T_g (°K)	I_{SAXS}
0	0.84	320	1.73
2	0.95	315	1.41
4	1.16	321	2.16
6	1.66	320	4.05

The sample with zero precure time was taken as the control. As shown in the data above the compositional fluctuation correlated with the toughness. It is also noteworthy that the value of T_g stays unchanged. Furthermore, there was no indication of a second low temperature T_g corresponding to the separation of the D-2000 phase.

In summary, this work demonstrates that the toughness can be increased without lowering the T_g by optimizing the processing conditions. The relation between compositional fluctuation and toughness observed in the present work needs to be verified in other systems before being accepted as a general rule.

Small Angle Neutron Scattering of Precursors to Gel Spun Fibers

Polyvinyl alcohol fibers with high strength and modulus have been manufactured via a reactive gel spinning process. The formation of alkaline gels is an essential intermediate step for this spinning process. The term "alkaline gel"

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

refers to PVA aqueous solution containing borate ions at a pH higher than 10.0. Without borate ions and high pH, the PVA aqueous solution will gel, but at a much slower rate; the gels so formed are called hydrogel. The objective of this work is to determine the change in PVA molecular conformation across the sol-gel transition in alkaline gels. This transition is thermo-reversible and rather well defined at a macroscopic level, e.g. by viscosity measurement.

Samples with different polymer molecular weight and concentration have been studied using small angle neutron measurements (SANS). The following observations have been made:

1) The sol-gel transition is observed in SANS as a sudden change in the zero angle intensity. The SANS transition however is about 20°C higher than what is observed via macroscopic measurements. This is consistent with what is known in percolation theory as the finite size effect.

2) In the sol region, the correlation length is always greater than the radius of gyration of the individual chain. This result suggests that the PVA solution in the semi-dilute region is not homogeneous. Molecular clusters persist at temperatures above the sol-gel transition.

(3) In solutions of polymer near the concentration C^* where the chains start to overlap one another, so-called critical behavior was observed near the sol/gel transition. This critical behavior is manifested by a change in the correlation length with temperature; the length reaches a maximum at the sol/gel transition. Such behavior is absent for solutions with concentrations greater than C^*.

Characterization of Polyquinoline Block Copolymer Using Small Angle Scattering Techniques

Polyquinoline is a major candidate for molecular composites. In a molecular composite, rigid rod molecules are dispersed in a matrix of a flexible polymer. The molecular rods act as the reinforcing fiber. Molecular composites have the potential to combine the performance of a composite, the easy processing of thermoplastics, and excellent properties at high temperature. In the ultimate molecular composite each molecular rod should be completely surrounded by flexible polymer molecules. There is, however, a strong tendency for the rigid rod molecules to aggregate and separate on a larger scale. To overcome this problem a number of modifications to chemical compositions are being explored. There is however a need to develop test methods to characterize the degree of dispersion in these materials so progress can be quantified. The work here is aimed at demonstrating that small angle scattering (SAS) is a viable technique for the structure determination in the solid state. The presence of microvoids has hampered the use of SAS for quantitative measurements of rigid rod polymers systems and their blends. To circumvent this difficulty, both small angle neutron and x-ray experiments were carried out on the same specimen. Due to the differences in the scattering contrast factors of the voids between x-ray and neutron scattering, the void contribution to the scattering intensity can be determined and removed.

To evaluate this potential measurement method, a block copolymer of alternating flexible segments of polyquinoline was studied. This is a promising system for molecular composites since the block copolymer nature of the material may help to promote good dispersion (the rigid and flexible segments substitute for the rod and matrix molecules). The average molecular weight for each block was about 17,000. Based on the density values for the copolymer and the two homopolymers, the following contrast factors for the scattering intensity I(q) of the deuterated block copolymers can be obtained.

$$I_{SAXS}(q) = 9.23\ V(q) + 3.37 \times 10^{-2} S(q) \qquad (1)$$
$$I_{SANS}(q) = 0.855 V(q) + 9.46 \times 10^{-2} S(q) \qquad (2)$$

where V(q) and S(q) are the structure factor of voids and block copolymers respectively. The values of I(q) for both SAXS and SANS were reduced to the absolute scale.

Both quantities are expressed in terms of the molar volume of the repeating unit of the rigid rod segment, and its value is 6.995×10^{-22} cm^3. The calculated molecular structure factor and the void scattering are given in Figure 1. The abscissa of this figure is Q, the magnitude of a scattering vector defined in its usual way; the ordinate is the form factor of the void and the block copolymer in Fourier space. Based on the peak height of the molecular structure factor, it is concluded that the block copolymer was not phase segregated; however, a strong intermolecular correlation was observed for each block. In other words, in the vicinity of a rigid chain the probability of locating another rigid chain is greater than its volume fraction. The same statement applies to the flexible chain also.

Crystallizable Thermoplastic Matrices for Composites

Thermoplastics offer important advantages as matrix resins for composites. The toughness and processibility of thermoplastics are particularly attractive, but some of these materials are also sensitive to attack by fluids. One approach to solving this problem is the use of partially crystalline materials since the crystallinity often improves resistance to fluid attack. To pursue this approach, however, it is important to learn more about the crystallinity in these resins and how it can be controlled. Poly(phenylene sulfide) (PPS), whose melting temperature is about 300°C, is being used in initial studies to address these questions.

The current and projected studies on the crystallization and morphology of PPS fall into two main groups, namely: (i) Investigations of the basic fine structural characteristics of the polymer, and their dependence on the molecular parameters and crystallization conditions, and (ii) Investigations of the influence of the carbon fibers on the crystallization behavior and orientation characteristics in the PPS matrix due to enhanced nucleation, if any, at the polymer/fiber interfacial regions. The information derived from part (i) of these studies is intended as background for determinations of processing/structure and structure/property relationships of the PPS per se while part (ii) addresses effects important in the composite.

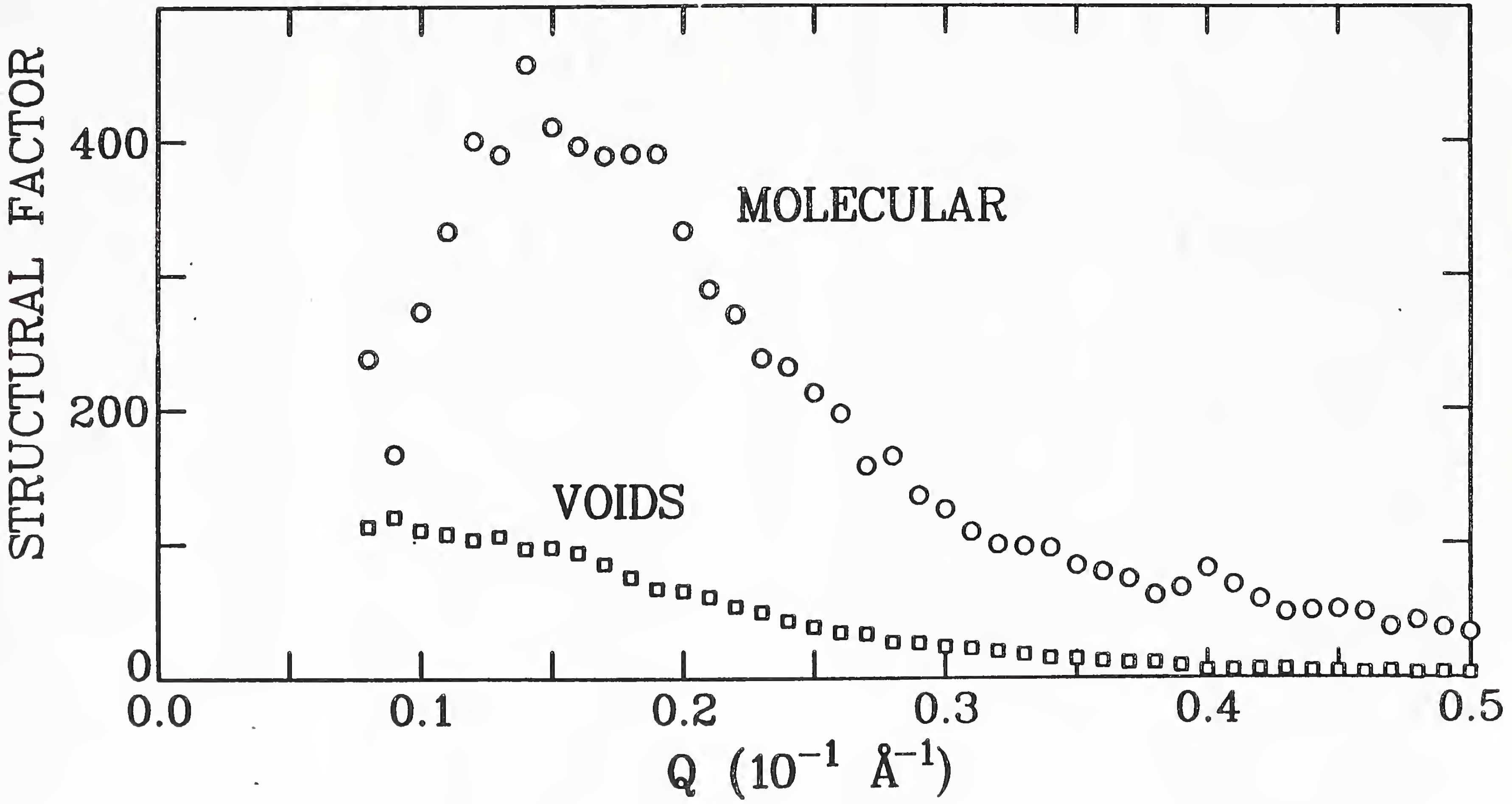

Figure 1: Form (or structure) factor for voids and the block copolymer plotted against the magnitude of the scattering vector, Q.

A focus in the current work is the study of the growth habits of single crystals of this polymer with the object of determining the fundamental characteristics of the process of chain folding. The unit cell of this polymer is orthorhombic, and it is known that the b-axis is the preferred growth direction in crystalline lamellae grown from solution, and in the constituent lamellae of spherulites grown from the melt. Important details of the growth and fine structure of the lamellae remain to be elucidated. Among these details is the question of whether or not the apposition of chains in a folded conformation occurs preferentially along specific crystallographic planes at the lateral faces of the lamellae during growth, or whether these faces are 'rough' at the molecular level. The latter possibility would entail crystallographically less specific folding and, in the extreme, the absence of sectorization in the lamellae. These alternatives bear importantly on the nature and extent of disorder in the lamellae and hence on the physical properties of the polymer; they are also basic to current debates concerning the role of surface nucleation (secondary nucleation) in the kinetics of the lateral growth of polymer crystals.

Experiments on the effects of melting conditions on the density of primary nucleation in PPS crystallized from the molten state have established conditions (melting at 300 °C, crystallization at 275-280 °C) under which lamellar single crystals were grown in thin polymer films (i.e. in the range 10-100 nm thick). A detailed transmission electron microscopical study of the crystals is under way. The crystals are multilayered. The basal (leading) lamella exhibits an overall lenticular lateral profile with an aspect ratio of 6-7. No distinguishable microfaceting could be resolved along the long and seemingly curved edges of these lamellae, neither could any faceting be distinguished at the extremities of their long axis. Dark field electron microscopy and decoration techniques are being used to probe the fold domain structure (sectored character) of the lamellae with the object of determining whether or not chain-folding in these crystals occurs preferentially along particular crystallographic planes. It should be emphasized in this latter connection that previous studies of polyethylene crystals in this laboratory and elsewhere have shown that the absence of crystallographically specific lateral faceting in lamellae need not entail the absence of preferential folding along certain planes.

Performance

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The main thrusts of the research effort on mechanical performance was material and structural aspects of damage tolerance. In the first phase, experiments were carried out to elucidate the material aspects of failure (such as fracture toughness and the effect of matrix ductility on damage zone characteristics). Utilizing this information analytical models were developed that predict the growth behavior of the flawed region. In particular, the analysis shows how the failure stress can be increased by altering design parameters such as fiber orientation, delamination size and shape, and fracture toughness.

Physical Aging of Epoxy Networks

Physical aging studies were performed using model epoxy network glasses. Linear and nonlinear viscoelastic responses were measured after quenching the glass from above T_g to the temperature of interest. In the linear viscoelastic regime, the effects of crosslink density on physical aging were studied. The stress relaxation curves at different aging times, temperatures, and crosslink densities could be superimposed to form a single master curve, demonstrating the validity of a time-aging time-crosslink density-temperature superposition principle for this type of epoxy network. Furthermore, at temperatures of 10°C and 5°C below T_g, the network glasses could be aged into structural equilibrium, thus obtaining, t^*, the time required to reach structural equilibrium. Results in the nonlinear viscoelastic regime showed that although the aging-time shift rate decreased as the applied stress increased, t^* did not change with the applied stress level. Consequently, aging is not "erased" by large mechanical stimuli. On the contrary, the results support the argument that the volume recovery which occurs during aging impacts the small deformation response differently than it does the large deformation response.

Effects of physical aging on the fracture toughness of epoxy network glasses were also investigated. In the preliminary study, the fracture toughness decreased as the time after a thermal quench, i.e. aging time, increases. Currently the relative importance of crosslink density, degree of aging and proximity to the glass transition in the fracture behavior of these network glasses is being studied.

Compression Strength: Analysis of a Single Fiber

Recently, there has been a growing interest in the research and development of organic fibers for use in advanced aerospace structures. A leading drawback of current fiber products is their low compressive strength which, unlike traditional glass or carbon fibers, is typically only a small fraction of their tensile strength. Morphological studies suggest that this critically-reduced strength arises from the peculiar structural makeup of the fiber. Such studies show that the fibers are made of highly-oriented, fibril-like elements which may vary in size from a few nanometers (microfibril) down to perhaps the molecular dimensions. Because these elements are only loosely held together (either by secondary bonding forces or a network of discrete interconnections), fiber disintegration can easily occur when interfibrillar stresses are present. A post-microbuckling analysis was developed to account for the low fiber compressive strength. The analysis, based on a concerted microfibril buckling induced by interfibrillar shear stress, identifies the geometric and material parameters responsible for fiber compression strength. Of these parameters, microfibril thickness and interconnection distance, both of which are set during fiber coagulation, figure prominently.

Interlaminar, Adhesive Bond, and Bulk Resin Fracture

An extensive experimental effort has been carried out to characterize the energetic and morphological aspects of interlaminar crack growth in composites, adhesive bonds, and bulk resin samples. Careful experimentation aimed at elucidating the crack-tip damage zone characteristics was performed using tools such as real-time movies or video recordings and post-mortem scanning electron microscopy. The results helped to explain the similarities and differences in fracture behavior for bulk resin, adhesive bonds, and composites.

Interlaminar fracture tests on composites are marred by a number of complicating factors such as fiber-bridging (the extension of fibers across the crack opening behind the crack tip), interfacial (fiber/matrix) vs. cohesive failure, and nonlinearity of the load-deflection curve due to matrix plasticity. In addition, sample fabrication and testing are time consuming and large amounts of resin are required, particularly when parametric studies (such as temperature, moisture and rate effect) are of interest. To meet this challenge, an alternative testing concept based on the fracture of thin adhesive bonds is being developed. In this test, the resin matrix is sandwiched between two metal adherends, with the bond thickness being similar to the interlaminar spacing in laminated composites. Figure 2 shows a comparison between the mode I fracture toughness for the bonded joint and that of the composite for three different resin systems: a brittle epoxy, toughened epoxy, and a thermoplastic. Although the results are limited, the agreement is excellent. The success in the mode I composite - adhesive joint correlation has led to an extension of the work to mode II (forward shear) and mode III (anti-plane shear) fracture components. Preliminary comparisons here are also encouraging.

Analysis of Laminate Compression Failure

Near-surface interlaminar defects, whether they are induced by foreign-object impact in structural composites or during fabrication in electronic circuit boards, are very detrimental to compressive strength. Under such loading, the (thin) delaminated layer buckles, causing intense stresses at the disbond boundary which may lead to structural disintegration at loads well below the design level. An analytical model was developed to predict the growth conditions and growth behavior of the debonded region as a function of the geometry and materials characteristics of the problem. The model assumes that the delaminated region is elliptic in shape and separates a thick isotropic plate from a thin orthotropic layer whose material axes coincide with the ellipse axes. The growth conditions and growth behavior of this defect are studied by separating the overall problem into an elastic stability problem and a fracture problem. Post-buckling solution for the elliptic section was obtained using a Rayleigh-Ritz type approach, with enough displacement terms being incorporated to ensure convergence of all field quantities of interest. The fracture problem was studied using a Griffith type energy balance criterion based on a self-similar disbond growth. The analysis identifies explicitly the role played by the experimentally determined interlaminar fracture toughness, and points to novel means for increasing strength through variations in stiffness properties of the delaminated layer.

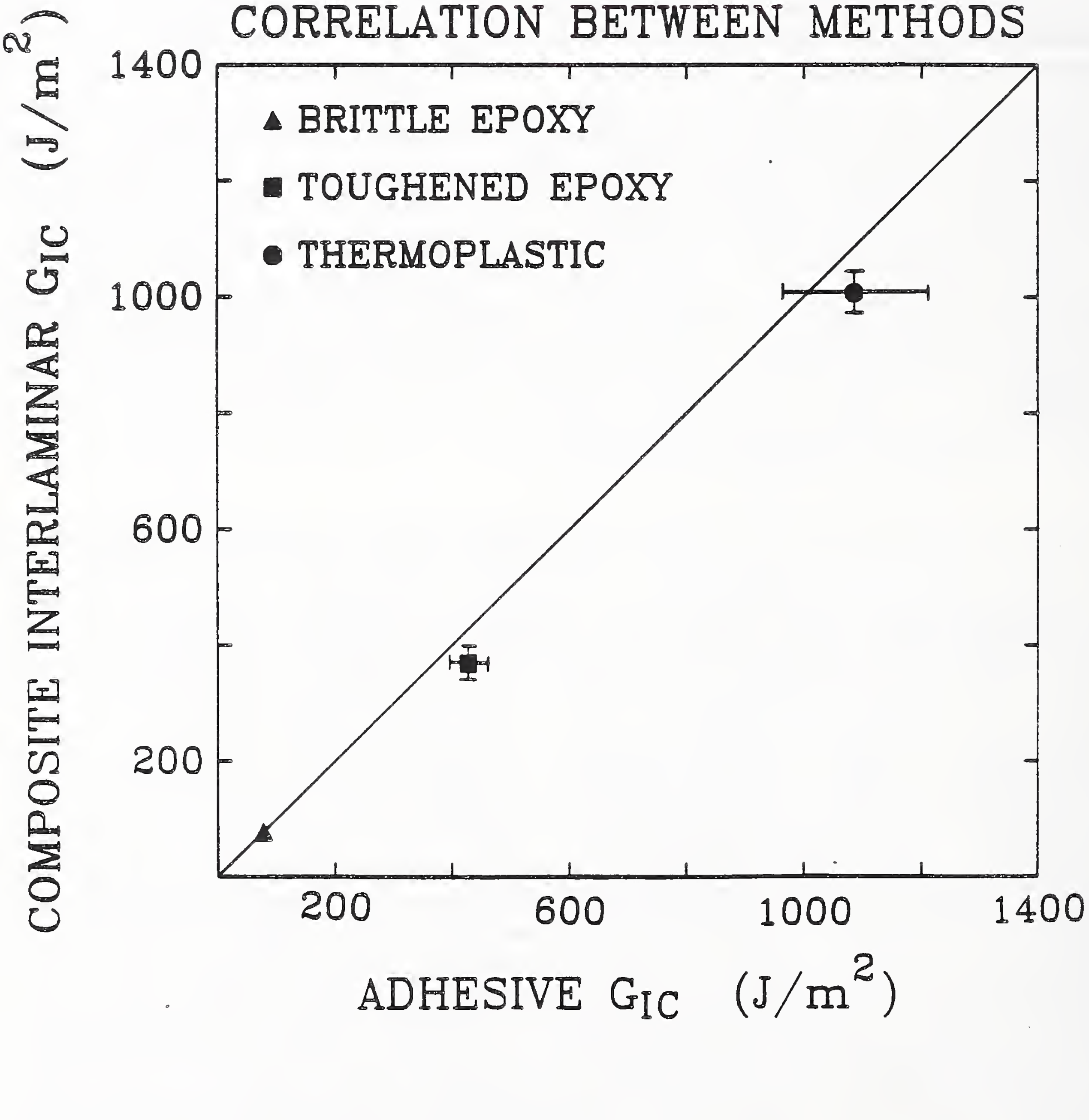

Figure 2: Comparison of adhesive and interlaminar frac energies for three different matrix resins.

Draft Standards for the Identification of Polymer Matrix Composite Materials and for Reporting of Test Results

Draft standards for the identification of polymer matrix composite materials and for reporting of test results are being prepared in an effort supported by the strategic defense initiative office (SDIO), in cooperation with the ASTM Committee E49, the Military Handbook 17 project, and DOD contractors concerned with data on advanced composite materials. The draft standards will be available for use by ASTM and others. The following existing data bases for advanced composites were examined in text form, discussed with their creators, or studied by participation in meetings aimed at the design or improvement of the database:

a. Prototype Advanced Materials Data Base User's Guide (PDA)
b. Data documentation requirements for MIL-DHBK-17
c. Guidelines and electronic data formats for reporting tensile property data and test conditions for fiber reinforced polymer-matrix composites per ASTM standard test method D3039 for fiber-resin composites. (PDA)
d. Data on the thermal expansion of graphite-epoxy composite in HTMIAC's high temperature materials properties data base.
e. Data on the ultimate tensile strength under rapid loading conditions of graphite/epoxy composite in HTMIAC's high temperature materials properties data base.
f. Format used by Martin Marietta Astronautics Group to present materials property data on composite tubes and plates to the Composite Materials and Applications Division of AMETEK.
g. Draft of SDS Spacecraft Materials Selection Guide for spacecraft design engineers presented by AMETEK. This Guide contains standardized tables of physical, mechanical and thermal data for composite materials.

Examination of these data collection formats revealed many points of view, many groups of data users, a complex set of interrelations, barriers to conceptually simple interactions, and many other interesting facts.

Based on this it appears desirable to describe a comprehensive data base containing all information about advanced composites, a facility for extracting subsets of information that are of interest to identified groups of users, and a number of specialized data bases, each to serve one of the identified user groups. The draft standards are aimed at facilitating the collection and smooth flow of information from where it is generated to where it is used, as well as the evolution of the data bases themselves.

POLYMER BLENDS

The importance of the subject of polymer blends is self evident by its ubiquitous presence in consumer products in resent years. These products range from automobile and airplane parts, furniture, packaging materials, housewares, toys to clothing materials.

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

Although miscibility in polymer blends is neither an absolute requirement nor always desirable, 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, and the barrier property, 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 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 in the group 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 used in polymer blend studies. A flow device which allows SANS study in situ has been constructed and used to study polymer blends under various shear conditions. A similar device for light scattering which will allow an extension of the study to structures of larger size is currently under construction.

Fy 88 Significant Accomplishments

- A new procedure for obtaining the temperature, composition, and molecular weight dependence of the free energy of mixing for polymer blends has been established. This procedure, which integrates the experimentally obtained interaction parameter χ with theoretical calculations to obtain a parameterized free energy function of mixing, has been demonstrated by using a binary polymer blend of polystyrene/poly(vinylmethylether).

Spinodal and cloud point curves have been generated and found to compare favorably with experiment.

- The effect of crosslinks between unlike chains in a blend to increase the compatibility has been studied by SANS technique. Blends of polystyrene/poly(vinylmethylether) subject to radiation dosage of 125 MRad have shown an increase of the single phase region of over 250°C.

- A renormalization group treatment of polymers interacting with surfaces and with excluded volume has been developed. This theory predicts that as a polymer expands due to excluded volume the probability of surface contacts becomes diminished so that surface interactions have a reduced effect on the molecular dimensions. This calculation requires a technical generalization which is relevant to numerous situations where polymers are subject to multiple interactions.

- The 10-meter small angle X-ray instrument has been operated as a user facility successfully. Basic construction of the instrument has been completed with the installation of a turbomolecular pump for the x-ray generator and a beam intensity monitor. Besides in house uses, six different external academic and industrial organizations have used the instrument for studies ranging from crystallization kinetics to microstructures determination in engineering plastics.

Experimental

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Temperature, Composition and Molecular Weight Dependence of Binary Interaction Parameter of Polystyrene/Poly(vinylmethylether) Blends

The technical importance of polymer blends has been well recognized in recent years. Making polymers miscible through chemical structure modification is a very important topic, but miscibility may not be the ultimate characteristic one is looking for. This is because synergistic effects which enhance the property of a phase separated material mainly come from molecular alignment, reinforcement, phase domain size and morphology.

In order to understand and possibly control the domain sizes and morphology due to phase decomposition, one has to understand thermodynamics (statics) as well as phase separation kinetics (dynamics). We understand that statics and dynamics are inseparable subjects if we wish to talk about phase behavior of even a simple binary system. The most important quantity needed in both static and dynamic characterization is the free energy (of mixing) of the system as a function of temperature and composition. For the case of polymer systems, we also need to know the molecular weight dependence of the free energy function.

Small angle neutron scattering (SANS) has been used to measure the effective or scattering binary interaction parameter, χ_{scatt} for a deuterated polystyrene/poly (vinylmethylether) (PSD/PVME) system. This technique offers a rather simple, fast and accurate method of obtaining the χ_{scatt} parameter. Therefore, a systematic study of this χ_{scatt} parameter as a function of composition, temperature and molecular weight has been carried out.

This measured χ_{scatt} can be related to the Flory-Higgins χ_F-parameter through thermodynamics relationship if the χ_F is allowed to be composition dependent. Then, through the compositional dependence of χ_F, the free energy function of mixing has been constructed. Spinodal temperatures and cloud point curves have been generated which compare favorably with experimental values.

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 changes of the hard segment domains upon deformation by small angle x-ray scattering (SAXS). As the sample is stretched in uniaxial tension the hard segment domains which are initially isotropically arranged begin to orient perpendicular to the deformation direction. At about 200% stretch the domains begin to break down and the distinct SAXS intensity maximum observable up to this point begins to decrease. At very large deformations (>400%, just before failure of the specimen) a new component to the scattering can be observed at very small angles oriented normal to the stretch direction. Simultaneously the sample starts to become opaque. Closer observation with an optical microscope indicates that the sample is beginning to craze. This behavior of crazing shortly before failure has been observed for all the polyurethanes studied up to this point.

SANS of Single Phase Interpenetrating Polymer Networks (IMN's)

We are studying phase separation behavior of single phase IPN's by small angle neutron scattering (SANS). The work which was originally centered on blends of linear poly(vinyl methyl ether) (PVME) and crosslinked deuterated polystyrene (PSD) has been extended to systems containing mixtures of linear protonated polystyrene (PSH) and crosslinked deuterated polystyrene. These PSH/PSD systems tend to phase separate at even lower crosslink densities than the PVME/PSD system indicating that to make compatible IPN's a negative value of χ (as found in the PVME/PSD system) is a necessity (i.e. requires starting with a compatible polymer blend before crosslinking). These results point out the strong effect of the elasticity of the network that must be included in the free energy of the system after crosslinking and which destabilizes the system (causes phase separation) even for normally miscible polymer blends.

SANS of Crosslinked Polymer Blends

Work has continued on the phase separation behavior of miscible polymer blends crosslinked by gamma rays. The effect of introducing crosslinks between the unlike chains in the blend is to increase the compatible region of the phase diagram. The blend system studied is poly(vinylmethylether) and deuterated polystyrene which is examined by SANS to measure the static structure factor as a function of temperature. Recent work has extended the studies to cover a wider range of radiation dose (up to 125 MRad). At the largest dose the effect on the phase diagram is to increase the single phase region by over 250°C. Extensions of this work are planned to study the effect of deformation and swelling in selective solvents on the phase separation.

Neutron Scattering Studies of Lipid Tubules Formed From a Polymerizable Surfactant

Small angle neutron scattering (SANS) and wide angle neutron diffraction studies have been initiated to determine the structure of tubules formed by the polymerizable lipid, 1,2-bis(10, 12-tricosadiynoyl)-sn-glycero-3-phosphocholine. A conversion from spherical liposomes to hollow, thin-walled, cylinders (tubules) occurs as the lipid is slowly cooled through its chain melting phase transition temperature.

Preliminary SANS and wide angle measurements have been made on suspensions of tubules and shards in D_2O. A pronounced peak can be observed for tubules in D_2O by the SANS experiments which gives the bilayer spacing. No obvious diffraction signal has been detected from the wide angle measurements conducted on the same material. This supports the notion that, due to the tight crystal-like packing of the lipid chains, water is completely excluded from the hydrophilic region. Therefore, there is no scattering contrast between the lipid chains to give neutron diffraction signals.

SANS measurements have also been initiated on partially deuterated lipid chains in tubule form. Results will be compared with model calculations of the scattering function, S(q), determined for various packing arrangements of the hydrocarbon chains.

Effects of Shear on Polymer Blend Critical Phenomena

SANS has been used previously to examine the critical behavior of quiescent polymer blends. An apparatus for observing the effect of shear *in situ* at the NBS SANS facility has been designed and constructed. Preliminary results on polystyrene/polybutadiene/dioctyl phthalate show an apparent increase in scattering intensity in the q-region studied by SANS, as shear rate increases for temperatures below the cloud point (2-phase region). Above the cloud point, no change in the scattering intensity is observed. Under no condition is any evidence of anisotropy observed. Work is continuing on this system as a function of molecular weight, PS/PB ratio, and total polymer concentration. Work has also been initiated on the design and construction of a light scattering apparatus for shear systems to provide complementary information.

Theory

E. A. Di Marzio, J. F. Douglas, C. M. Guttman

The Free Energy Density of Curved Crystalline Membranes

The Helfrich form for the free energy of curved membranes is shown not to be applicable to crystalline membranes. The Helfrich form is shown to derive from the Frank-Oseen expressions when only the splay part of the curvature tensor is non-zero. The Frank-Oseen (and also deGennes-Ericsen) free energy expressions are valid only for liquid membranes. To obtain a more general expression applicable to crystalline membranes one must obtain invariant forms by contracting both the director **L** (and its spatial derivatives) and the displacement vector u (and its spatial derivative, the strain tensor ϵ_{ij}) with the 4 indexed symbols C_{ijkl} characterizing the symmetry of the lattice. There are 7 different kinds of cross terms that can be formed by contracting the director **L**, the displacement vector **u**, and their first derivatives with the structure constants of the membrane. They are being examined to see which ones describe curved membranes.

The Dimensions of Star Molecules

The dimensions of a star molecule are easily estimated by a modification of the Flory counting scheme. The results for the expanded polymer were shown to be the same as the Cotton-Daoud results (1.2 power of molecular weight and .40 power of the functionality). We have now been able to estimate the prefactor as 1.74. This compares with 1.84 obtained from Monte Carlo modeling.

The Glass Temperature of Rings

The glass temperature of polymeric rings is obtained from first principles for polyvinypyridine and shown to agree with measurements of Hogen-Esch and Toreki. The glass temperature of mixtures of rings and linear polymers of the same species and molecular weight is shown to be a linear function of the weight fraction of the rings.

Polymer Localization by Random Impurities

Simple dimensional analysis is employed to discuss the relevance of impurity interactions on the molecular dimensions of flexible polymers in the limits of high and low impurity densities. By exploiting an analogy with electron localization in disordered materials it is found that the presence of random obstacles generates a net attractive interaction of the polymer for itself which ultimately leads to chain collapse at a critical density of impurities. Theoretical predictions agree well with recent Monte Carlo simulations. It is suggested that the contraction of molecular dimensions, which sometimes occurs upon heating polymer solutions, can be understood as arising from density fluctuations ("impurities") in the solvent. The random impurity model is also qualitatively useful for understanding how a non-homogeneous environment affects the mean molecular dimensions in numerous more complicated but practically interesting problems such as gel chromatography, polymers at rough interfaces, etc.

Flexible Polymer with Excluded Volume at an Interacting Surface

A renormalization group treatment of surface interacting polymers with excluded volume requires a technical generalization which is relevant to numerous situations where polymers are subject to multiple interactions. The theory predicts that as a polymer expands due to excluded volume the probability of surface contacts becomes diminished so that surface interactions have a reduced effect on the molecular dimensions. A similar effect was previously found in di-block copolymers where an expansion of the blocks diminishes the effect of the interblock interaction.

Characterization of Branching Architecture Through "Universal" Ratios

Experimental and Monte Carlo data for dilute solution properties of "lightly branched" polymers (Stars, combs, rings ...) are compared with the renormalization group predictions of Douglas and Freed. "Universal" dimensionless ratios for the mean dimensions of lightly branched polymers, relative to linear polymers having the same molecular weight, are stressed since these ratios are useful in characterizing branching architecture. The reason for the weak dependence of these dimensionless ratios on solvent quality is described on the basis of the renormalization group theory. Subtle complications associated with hydrodynamic solution properties and with the effect of ternary interactions upon theta-point chain dimensions are briefly discussed. A comparison between theory and experiment is also made for dimensionless ratios involving the polymer second virial coefficient A_2.

SAXS and Pole Figure Facilities

Digital Camera for Small-Angle X-Ray Scattering

The SAXS facility has been in routine use for over a year. Internal NIST users have made extensive use of the facility to study topics ranging from matrix structure of composites to metal uptake by bacteria. Six different external academic and industrial organizations have used the instrument for studies ranging from crystallization kinetics to microstructures in engineering plastics.

Basic construction of the instrument was completed with the installation of a turbomolecular pump for the x-ray generator and a beam intensity monitor.

Calibration measurements for establishing an absolute intensity scale are currently underway.

We are currently constructing a computer-controlled heating stage for high temperature studies. This will be used to study scattering from blend systems in the single-phase and phase-separated regimes as well as crystallization kinetics of semicrystalline polymers, microphase structure in block copolymers, and similar topics.

X-Ray Pole Figure Facility

Extensive measurements have been made on blown films of polyethylene by scientists from the Mobil Chemical Co. R & D labs. These measurements have illustrated the need for numerical methods for calculating crystallite orientation distribution functions from pole figure data.

In conjunction with the University of Virginia we have modified the data collection software on the pole figure facility to permit collection of data for crystal structure determinations from fiber specimens.

DENTAL AND MEDICAL MATERIALS

The objective of this Group is to provide basic materials science, engineering, and test methods which may be used by sectors of the health-care industry for the development of new or improved materials, delivery systems, and standards. Although no current effort is in progress on diagnostic systems, plans do include these activities for the future.

Materials-research efforts, aimed at development of materials and techniques for promoting adhesion to tooth, dentin, enamel, bone, and soft tissues, are pursued for reducing marginal leakage of restorations 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. The durability of dental materials is investigated by pin-on-disc wear studies and by characterization of aged materials by the application of the Weibull method of statistical analysis. Studies of calcium phosphate compounds for endodontic sealants, bone augmentation, or caries-reducing agents are being investigated. The basic chemistry of precipitation of calcium phosphates is explored as it relates to formation of mineral deposits such as bone, teeth, and atherosclerotic plaque.

Theoretical and experimental studies of stresses within bonded dental systems are explored with the objectives of defining the most compatible material-property and geometrical design combinations for porcelain-to-metal, tooth-to-resin, resin-to-filler bonding and so forth. Characterization 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 published with a view toward improved alloys and processing methods.

FY 88 Significant Accomplishments

- Initiated three monthly series of communications with dental industry-trade-profession.

- In the study of spiro orthocarbonate monomers capable of double ring-opening polymerization with an expansion in volume, a novel monomer was prepared which exhibits reactivity comparable to conventional methacrylate monomers and high ring-opening efficiency at near ambient polymerization conditions.

- A novel dental restorative, a hybrid cement-composite, has been developed in order to overcome the propensity of conventional glass-ionomer cements to brittle fracture during wear from occlusion. The restorative involves the usual hardening of a commercial glass-ionomer cement along with the polymerization of a water-soluble monomer (e.g. hydroxyethyl methacrylate) incorporated in the system to provide toughening. *In vitro* tests revealed good wear resistance, excellent oral-environmental resistance, and no catastrophic failure during wear.

- Newly synthesized low molecular weight polymers prepared from vinyl and isocyanate containing monomers adhere at least as well to glutaraldehyde treated dentin than the most efficient dentin bonding agents, thereby providing another potential alternative bonding system for dental applications.

- An "ultrasimplified" two-step system for bonding dental resins to hard tooth tissues has been developed, streamlining a multistep procedure developed by ADA Health Foundation research associates in 1981.

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

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A study was initiated to measure the effect of the submersion of dental composites in 70% ETOH for a prolonged period of time (up to 6 months). In order to adequately characterize the material using a Weibull distribution, 60 samples were made for each of 4 time intervals. In a related effort the effect of filler content on the Weibull modulus of an experimental composite resin is being studied. A resin/powder ratio of 0.20, 0.25, 0.50 as well as unfilled resin has been used to make 60 samples of each composite to determine the Weibull modulus and the characteristic strength.

Studies were continued on the development of an experimental dental composite restorative containing a fluorinated flexible resin in an attempt to improve wear and oral-environmental resistances. A dual cure (chemical and visible-light activated) was employed to increase the degree of cure, which is viscosity limited. Wear tests on these composite specimens preconditioned in food-simulating liquids revealed good environmental resistance; however, the wear rate was still larger than desired.

In collaboration with the University of Maryland Dental School, studies are being continued on the influence of various topical fluoride-gel treatments on selected commercial dental composites. These studies involve in vitro wear tests (NIST), weight losses from gel treatments, microdefect analysis, and clinical tests. In cases where significant weight losses were observed, the in vitro wear resistance often improved. SEM studies on these specimens revealed polymer-rich layers on the wear tracks, which apparently resulted from portions of inorganic filler being etched out by the gel treatments. During wear the voids were filled with residual resin, which apparently provided a lubricating effect.

In collaboration with the Naval Dental School the wear of human enamel against a commercial castable-ceramic restorative materials was measured. This quantity was compared to that for enamel wearing against a conventional porcelain, used as a control. There was no significant difference between the enamel wear from the castable ceramic and porcelain, which means that the former is satisfactory in this respect. However,if the ceramic was shaded using a glaze provided by the manufacturer, the wear rate of the enamel increased by a factor of two. Accordingly, this glaze should not be applied to stress-bearing occlusal surfaces.

Preliminary measurements have been made to determine the amount of wear on synamel (sintered polycrystalline hydroxyapatite), used to simulate human enamel, against titanium. The wear from titanium is being compared with that using other commercial alloys which bracket titanium with respect to hardness. Paradoxically, the softest alloy, containing gold, produced the most wear on the synamel. The hard alloys, including titanium, tended to polish the synamel, apparently reducing friction, which, in turn, reduced the wear rate. More work is necessary, including improved microdefect analyses, to assess the various wear mechanisms and to determine the relevance to corresponding in vitro wear involving occlusion with enamel.

The development of a new, automated, pin on disc, dental-wear apparatus has continued. This apparatus will be able to make continuous wear measurements on specimens under selected media to simulate the intraoral environment.

A final progress report has been written and submitted for NBS review concerning high-temperature neutron-diffraction studies on the Ti-Al alloy system. Our studies have revealed the existence of short-range atomic ordering which is critically affected by small amounts of dissolved oxygen. We have also discovered a hitherto unknown high-temperature phase at about 40 atom-percent Al which appears to have a hexagonal close-packed structure.

Ongoing research into resin-modified glass-ionomer cements resulted in the development of two new types of these hybrid cement composites. One type is based on the use of an aqueous polymer solution (rather than just water or water plus tartaric acid) with the powder component of a water hardening glass-ionomer cement. Water soluble polymers such as gelatin, polyethylene oxide, polyethylene glycols, etc. were investigated. The resulting hybrid cement composites exhibited less propensity to brittle failure and excellent tensile strength. A second type also employed a water soluble polymer but in combination with a water-compatible, polymerizable resin. This type of formulation also yielded toughened hybrid cement-composites.

In the second phase of a NIDR contract to clinically evaluate the ferric oxalate-NPG-PMDM dentin-enamel adhesive system, more than 150 permanent restorations have been placed to permit clinical performance of these materials over three years. Most restorations required only hand instrumentation without anesthetic or cavity retention form. Application of this adhesive system to cementation of castable ceramics and desensitization of dentin are currently being explored clinically.

Techniques for shielding soft tissues adjacent to metallic dental restorations during head and neck radiation therapy have been demonstrated clinically during the past year. Current research is focusing on characterizing the dose-depth scatter enhancement of different restorative materials subject to different treatment energies. A simulating phantom has been designed to study restorative materials exposed to Cobalt 1.2 and Linac 4,6,10 and 20 MeV radiation sources.

Observations of single-tooth precision-cast titanium restorations in place after 34 months indicate some wear on opposing teeth. Epoxy models of these castings and teeth are being evaluated by direct profilometry to determine the location and extent of this wear. The clinical compatibility of these castings with oral tissues appears excellent at this time.

Clinical trials of class I, III and VI composite restorations using glass inserts have been successful in developing techniques and instrumentation for application and handling of the inserts. Newly formulated microcrystalline glasses are currently being investigated.

Medical Materials: Improved Tissue Adhesive and Improved Surgical Bone Cement

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To study the biocompatibility of tissue adhesives with pendant isocyanate groups, samples of oligomers and cemented bone specimens were sent to various laboratories (Northwestern University, University of Texas, El Paso, University of South Carolina, Indiana University, University of Regensbung, Germany, University of Manchester, England, University of Calgary, Alberta, Canada). A cyanoacrylate formulation was prepared for the Medical School, Vanderbilt University.

Over 20 new oligomers containing pendant isoyanate groups were synthesized from various vinyl monomers, m-isopropenyldimethylbenzyl isocyanate (TMI) and 2-isocyanatoethyl methacrylate. Dilute oligomer solutions adhere as well or better to glutorraldehyde treated dentin than other bonding agents and the soft tissue and dentin base resin. However, the formulations containing the previously synthesized methacrylate esters are the most efficient adhesives for bone. Bond strength does not depend on the isocyanate content of the oligomer and is independent of molecular weight.

Calcium Phosphate Chemistry, Biochemistry, Structure and Clinical Implications

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Chemical and crystallographic investigations of octacalcium phosphate (OCP), a precursor in the formation of tooth mineral, and its role in biomineralization have continued. The OCP-dicarboxylate system was studied, including simple dicarboxylic acids and several derivatives such as amino acids and unsaturated acids. Preliminary results indicate the incorporation of fumarate ions into OCP. Attempts to prepare single crystals of these complexes suitable for structural studies are continuing.

The maturation of amorphous calcium phosphate (ACP), that is, the transformation of ACP to crystalline apatite, was studied by monitoring the change in crystallinity, using x-ray powder diffraction. A study of the process indicates the formation of an intermediary phase, which appears to be OCP. Results of the study indicate that ACP has potential application for remineralization and/or fluoridation.

Investigations of demineralization and remineralization of dental specimens using synchrotron radiation and x-ray magnification microradiographic techniques have continued. High-resolution microradiographs have been obtained of dental specimens of various thicknesses using a range of x-ray energies.

Apatitic fluoride content of tooth mineral was increased by treatment with a calcium phosphate solution containing complex fluoride compounds such as sodium fluorostannate and sodium fluorosilicate. A single treatment incorporated approximately 3000 ppm fluoride as apatitic fluoride. This process was also evaluated for effectiveness in remineralizing artificially formed lesions in enamel of extracted teeth. The procedure appears clinically feasible because of the relatively short treatment time.

Fluoride uptake from low level fluoride sources has been measured using a constant composition method without enamel biopsies. Results indicated absorption in fissures of extracted human molars from solutions containing as little as 0.05 ppm fluoride when activated by a dicalcium phosphate dihydrate-forming treatment.

Two constant composition methods were used for investigation of the labile and permanently bound fluoride uptake produced by topical treatments and the concomitant increase in tooth resistance to lesion formation. Fluoride uptake was highest and lesion formation lowest in a four-minute experimental treatment with dicalcium phosphate-forming solution followed by acidulated phosphate fluoride.

In vitro tests of the calcium phosphate cement developed by research associates in the ADA Health Foundation's Paffenbarger Research Center showed that it fills and seals root canals as well as or better than the gutta-percha/Grossman cement system now in wide use. Animal studies have shown that the cement causes no long-term detrimental effect on periapical tissues.

A study was made to determine whether a slurry containing equimolar amounts of tetracalcium phosphate and dicalcium phosphate dihydrate in water can effect remineralization of artificially formed lesions in the roots of extracted teeth. The procedure resulted in a substantial increase in mineral density in the outer 30 micrometers of the lesion and a smaller increase in the rest of the lesion. The treatment appears practical because the chemical nature and consistency of the slurry renders it safe and easy for overnight applications without using chemical retaining trays.

Microanalytical techniques were used to study the solubility of tooth enamel by measuring the compositions of dilute acid solutions placed in micrographic wells drilled into the sound and carious regions of tooth specimens. Carious enamel was significantly less soluble, probably because of loss of carbonate and other soluble constituents during caries formation. Residual apatite crystals might have higher fluoride concentrations which would make them less soluble in acidic solutions,.

Cardiovascular deposits may be represented as apatitic phases with substantial sodium, magnesium, and carbonate substitutions. They are formed by hydrolysis of octacalcium phosphate to a complex hydrolyzate. A systemic investigation of carbonate substituted hydrolyzates was undertaken. The findings provide new evidence that OCP is a precursor in formation of pathologic calcified deposits.

Further analyses of precipitated nearly-stoichiometric hydroxyapatites (HAs) indicate about one water molecule per unit cell is structurally incorporated in these HAs. Insufficient vacant lattice sites were found by chemical analyses to accommodate this water. Hence, the unit-cell symmetry may be distorted from hexagonal to spatially fit this water, and experiments are under way to test this hypothesis.

Acidic phospholipids (APL) help regulate mineral formation in matrix vesicles, the sites of initial calcification in many skeletal tissues. Results from model liposome studies suggest that this regulation is affected by the location of the APLs in the MV's covering bilayer membrane. Inside monolayer APLs delay the appearance of extravesicular mineral; external APLs delay subsequent growth. Results also showed that other membrane constituents can affect mineral development indirectly by altering the transmembrane APL distribution.

Several new types of fillers for dental composites based on calcium metaphosphate chemistry were developed. Calcium metaphosphate (CMP) is a unique phosphate mineral existing in four crystalline forms and one amorphous form and possessing a polymeric structure. The forms have refractive indices that are optically compatible with BIS-GMA type resins, thereby permitting their use in visible light activated composite formulations. In this study, crystalline β-CMP and vitreous CMP were prepared, ground to particle sizes between 1 and 25 um, characterized and then evaluated as fillers for composites using photoactivated resin systems. Depth of cure was of the order of 5-6 mm using 40 seconds of irradiation from a commercial blue light source.

Dental Polymer, Composite, Cement, Sealant, and Adhesion Chemistry

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Composites formulated with fillers of vitreous CMP expanded on storage in water but had relatively low strength, whereas those based on β-CMP were much more moisture resistant, stronger and showed a tendency to arrest brittle fracture. These novel fillers have potential application in a number of other resin based materials and dental cements.

A study was initiated to ascertain if the formation of hydroxyapatite occurs from tetracalcium phosphate (TTCP) and dicalcium phosphate (DCP) when the latter are contained in hydrogels formed by self-curing reactions. Hydroxyapatite formation occurred in hydrogels derived from poly(alkenoic acids) such as poly(acrylic acid) but not in hydrogels derived from 2-hydroxyethyl methacrylate with crosslinking monomers. The calcium polyacrylate cement that resulted from TTCP or TTCP/DCP shows promise as a dental cement.

To enhance the conversion of vinyl groups in dental resins several approaches are being pursued. One approach involves using highly reactive vinyl monomers such as α-methylene β-butyrolactone. Several substituted vinyl lactones have been synthesized that are expected to have, in addition to their high reactivity, improved solvent resistance and low polymerization shrinkage.

Still another method for improving the extent of polymerization involves developing more efficient initiator systems (e.g. dual cure initiators combining photochemical and chemical activation). Using several types of dual-cure initiators, significant improvements in the conversions, hardness, tensile strengths and solvent resistances of dental resins and their composites were obtained.

The study of monomers capable of free radical, double ring-opening polymerization with an expansion in volume has been focused on a particular spiro orthocarbonate system which optimizes both reactivity and ring-opening efficiency (and thereby expansion). An aromatic-substituted monomer has been synthesized which exhibits complete ring opening under all polymerization conditions investigated. This monomer also yields polymers with increased glass transition temperatures relative to previous ring-opened polymers.

In contrast to these spiro, ring-opening monomers, a new class of difunctional monomer which can polymerize by an intramolecular ring closure pathway are being synthesized and evaluated. By this process, polymers have been prepared in which quantitative conversion of the double bonds has been achieved. A project to determine whether this monomer can reduce the residual unsaturation in conventional composites is currently underway.

An alternate approach to improving both the conversion and chemical resistance of resin-based dental materials involves the use of highly reactive vinyl lactone monomers. A series of substituted methylene butyrolactones were prepared and polymerized to demonstrate that variation of the side chain functionality could drastically alter the solvent resistance of these non-crosslinked polymers. Polymerization shrinkage and glass transition temperature were also related to the substituents.

Work has continued on improving the adhesive bonding system developed by research associates in the ADA Health Foundation's Paffenbarger Research Center, (PRC), and on determining conditions for packaging, dispensing and storing the components. A two-step system that can be completed in less than two minutes greatly simplifies the treatment for both enamel and dentin and gives tensile bonds equivalent to the previous three-solution protocol.

Methods have been developed for testing adhesion and microleakage at temperatures closely simulating oral conditions. These new techniques allow determination of the effects of body temperatures on bond strengths and sealing abilities of esthetic restorative systems.

New monomers have been synthesized for protective tooth coatings. The first was the reaction product of pyromellitic dianhydride and 2-(N-tertbutyl) aminoethylmethacrylate.

Electron paramagnetic resonance (EPR) spectroscopic analysis revealed the presence of free radicals in ground enamel and dentin. This phenomenon will be studied to determine if free radicals in the instrumented tooth surfaces help initiate the "spontaneous" polymerization of the PRC developed adhesion system monomer.

Dental Alloys, Ceramics, Metrology, and Analysis

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A finite element analysis was conducted to explore the effects of material properties, cooling rates and thickness ratios for a three layered porcelain-opaque-metal slab. Results show high transient tensile stresses at the metal-opaque interface during cooling and high residual surface stresses cooling. The magnitudes may be altered by changing the thermo-physical properties of the materials involved.

Recent work has focused on designing more effective methods for casting titanium and the development of commercially feasible casting machines. These advances, coupled with the development of new casting investments and porcelain bonding techniques have made the production of titanium dental castings a viable commercial enterprise.

The development and study of alloy phase diagrams has shown that alloys of certain metals are especially promising for use in dentistry. The include hafnium, molybdenum, niobium, tantalum, and other less common metals which are relatively inexpensive. Work is continuing in analyzing alloy systems which exhibit ductile behavior, especially those having stress-induced transformations.

The use of the Weibull distribution has shown that for the diametral tensile strength data of one composite resin, more than one failure mechanism seems to exist. A mixed Weibull was found for the failure data with two distinct Weibull parameters. The characteristic strength remained unchanged.

The Weibull method of analysis was also applied to porcelain-to-metal system fracture data. The effect of two methods of reglazing on the overall system strength was measured. No major difference were observed but it was learned that a larger number of specimens is needed to discern secondary effects.

Preliminary results on resin bonded bridges placed at the University of Maryland Dental School have been used to determine a characteristic service life for that particular restoration by treating the data as a censored Weibull distribution of times to failure.

High temperature strain gauges have been embedded in phosphate bonded investments in order to determine the thermal expansion at the site of the wax pattern. The strain gauges recorded the onset of the phase transitions of the filler particles very reproducibly. Reversible phase transitions were observed on heating and cooling. The amplitude of the strain observed is several orders of magnitude larger than the strain gauges could tolerate, indicating that unexplained electrical signals are generated during the heating cycle which obscure the actual strain information.

Dental instruments and handpieces can be degraded by autoclaving and cold sterilization is not very effective against viral and spore mediated diseases. An investigation has begun using a microwave magnetron as the RF source for producing a gas plasma. Preliminary results have shown that bacterial spores can be inactivated by an exposure to the plasma of 10 minutes duration. Microwave radiation alone did not produce inactivation. The gas plasma caused severe heating of the vacuum chamber walls, which requires further investigation.

A modified composite bending beam is being designed for the evaluation of the resin-etched-metal system strength. A casting technique has been developed to produce the specimen with the particular dimensions.

A new electric arc furnace has been designed and constructed which will permit casting large dental appliances, such as partial dentures, from titanium-based alloys. Further testing will probably stimulate commercial activity in this field. Such devices will also be useful in the rapidly-growing field of dental implants where titanium castings can play a critical role.

OUTPUTS/INTERACTIONS

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World Biomaterials Congress
J. A. Tesk, Chairman, Session on Dental Materials

Industrial and Academic Interactions

Industrial

The Research Associate agreement with IMASS Corporation to transfer the time domain spectrometer technology for commercialization has resulted in an instrument which is offered for sale by the company. Capabilities of the instrument are equivalent to those of the spectrometer developed by NIST.

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

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

In collaboration with Chronos Research Laboratories, preliminary experiments have been performed on the laser-induced release of electrical energy from polarized films of piezoelectric polymers.

Over twenty industrial representatives from polymer processing companies were invited to the NIST Intelligent Materials Processing Workshop held on August 31-September 1, 1988. Those attending the workshop were from a cross section of the polymer processing industry including resin manufacturers, processors, machinery manufacturers, and end users. The workshop presented an excellent environment for the direct interchange of ideas and technological information between NIST and the polymer processing industry.

A recently inaugurated Research Associate collaboration with Technical Assessment Systems, Inc., installed and collaboratively demonstrated with Polymers Division staff, the first applications of ultratrace biosensing of organometals by in vitro computerized multilaser spectrophotometry and selected mutant strains of a bacterium. These results set the stage for field testing of a potentially new measurement system, applicable to relating molecular topologies of technological materials quantitively to both adverse and beneficial biotic responses.

Bioreduction of gold and other precious metals to pure metallic microparticles by volatile metabolic products was demonstrated. Reaction intermediates, morphologies and purity of particles were evaluated by scanning electron microscopy-energy dispersive x-ray microanalysis techniques. The work attracted an invitation from the Metallurgical Society and American Institute for Mining Engineering to present a talk on the subject at the upcoming International Symposium on Biotechnology in Minerals and Metals Processing. Several platinum group metals and catalyst industrial firms have now indicated collaborative interest.

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.

Discussions are in progress with members of ASTM D-20 subcommittee on thermal methods on the production of a polypropylene SRM for which the melt flow rate will be certified. This standard reference material will facilitate calibration of melt flow apparatus described in the voluntary standard method ASTM D-1238.

The Institute of Paper Chemistry, Appleton, WI. is collaborating with NIST in the study of the effects of diethyl zinc (DEZ) treatments on cellulonic materials. The Library of Congress funds the work in support of its program to use DEZ to enhance preservation of archival materials.

A joint research project on advanced thermosets has been initiated between NIST and Interez. High performance polymeric composites call for matrix resins with a high glass transition temperature and a high fracture toughness. Bisphenol A dicyanate (BADCy) from Interez is a major candidate for this need. Partially deuterated BADCy has been prepared by Interez, and the network structure of this material is being characterized by NIST using neutron scattering. It is of interest to compare the network structure for this new type of resin to that obtained for the epoxy systems previously studied in the NIST program.

Joint polymer blends related projects are underway with several large companies. These include Exxon, IBM, eastman Kodak, Hercules, Mobil Chemical and General Motors. The work will focus on equilibrium phase behavior and phase stabilization problems for specific polymer blends with Exxon, IBM and Eastman Kodak, and on the domain orientation, fiber structure and blends morphology with Mobil Chemical, Hercules and General Motors. The newly constructed 10 meter SAXS instrument has also been used by Mobil Chemical, Hercules and General Motors for structural characterization on various polymers.

Contacts with the dental industry and profession have remained strong. Monthly articles have been submitted to the American Dental Trade Association, the American Association of Dental Manufacturers and the American Dental Association to keep them abreast of recent developments. An invited lecture was delivered to the "Cal-Lab" group of dental laboratories on future dental laboratory processing methods. Research associate agreements with Dentsply International and Astron Corporation remain enforce and the latter has introduced a significantly new product as a result of its work at NIST. Assistance in materials or funding was supplied to NIST or the American Dental Association Health Foundation Research Associates at NIST by Pentron Corporation, Morita Corporation, the Colgate-Palmolive Company and Tokuyama Soda Company.

Industrial/Academic

The piezoelectric properties and molecular orientation of deuterated vinylidene fluoride polymers and copolymers supplied by AT&T Laboratories have been investigated in a cooperative effort between NIST and Washington University in St. Louis.

Metabolic products of fungi capable of solubilizing phosphorus from iron ore were identified in collaborations established under the NIST Steel Program. Tests with U.S. industrial iron ore concentrates showed the bioproducts, consisting of oxalic acid and other organic acids, rapidly (<10 min) removed over 50% of phosphorus from the ore and potentially offer a novel bioprocess for domestic iron ore beneficiation. More detailed evaluation of biological dephosphorization and potential on-site scale-up testing with Cleveland Cliffs Iron Co. and Michigan Technological University is planned.

The desulfurization of coal by extremely thermophilic bacteria (100°C) was demonstrated in a joint NIST-Johns Hopkins University project supported by the Electric Power Research Institute. The use of microorganisms to bioassay sulfur species in coal was also demonstrated. These data provide information on the types and accessibilities of forms of sulfur in coal and also provide novel processing options for coal beneficiation.

Researchers from Exxon Research and Development Company, Hercules, Inc. and the University of Pittsburgh are collaborating with scientists in the Polymers Division in characterization of dilute solution and melt properties of cyclic macromolecules. A manuscript has been prepared on the work which addresses validation of current models of macromolecular dynamics.

A joint NIST-Polaroid-Kyoto Institute of Technology (KIT) project has been initiated to determine the structure of polyvinyl alcohol (PVA) gel, more specifically the structure of alkaline gel. This type of gel is the precursor of high performance PVA fiber, and the properties of the fibers depend on the structure of the gel. Both gel and fiber samples are being provided by KIT and Polaroid while NIST is characterizing the structure of these materials.

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

Academic

Dr. Naoto Tsutsumi from Kyoto Institute of Technology is working at NIST during his sabbatical leave. He is studying changes in the spectra of molecular probes to measure internal electric fields in polymers.

Collaboration continues with the University de Nantes, France and the Universitas di Milano, Italy to explore the use of Resonance Raman Scattering to determine the effective conjugation lengths in polyacetylenes of different molecular weights.

In collaboration with IMSE guest scientists from Universities of Maryland and District of Columbia, a complete NBS computer program has been successfully demonstrated with capability to assess energetically likely molecular configurations and van der Waal "total surface area" (in A02) for quantitative structure-activity relationships (QSARs), applicable as independent predictors for both physicochemical and biological properties. With both ongoing NBS metals bioprocessing and external transfer of NIST QSAR data or methods, joint published results demonstrate ongoing metals solubility, chromatographic partitioning, biouptake and toxicity applications attracting substantial domestic and international collaborative prospects.

We determined experimental protocols and successfully demonstrated with the new NIST Cold Neutron Source application of small angle neutron scattering plus x-ray scattering techniques to characterize metal particles in and on living cells in collaboration with Professor R.P. Blakemore of the University of New Hampshire. Conditions necessary to conduct kinetic metal bioprocessing experiments have been established.

Collaborative work with J. Shibata, University of Tennessee, is being carried out for the purpose of employing fluorescence photobleaching and fluorescence quenching to measure polymer processing parameters.

Epifluorescence microscopic imaging (EMI) methods in combination with metal-specific fluorogenic ligands was used to demonstrate bioaccumulation of yttrium by bacteria and aluminum by plant material in collaboration with University of Maryland students. These demonstrations illustrate the potential of the method for trace monitoring of metals bioprocessing and mapping resident metallic moieties in biogenic or synthetic polymer composites.

A novel mechanism of microbial resistance to chromium (VI) was demonstrated in collaboration with Professor F. Baldi of the University of Siena, Italy. A chromium-resistant yeast isolated from tannery wastes was shown to exclude Cr from the cell. Further characterization of mercury resistance and biotransformations by aerobic bacteria isolated from Italian cinnabar deposits also showed that mercury resistance is not related to biomethylation. In this connection, NBS staff have been invited to a NATO-European Community meeting to provide guidance and transfer NBS measurement methods, standards and mechanisms involving the origin and fate of methylmercury in the Mediterranean.

The bioaccumulation of gallium by microbial cells and gallium binding by exocellular biogenic iron macrothelators, or siderophores, was demonstrated as part of an Air Force supported project to develop novel processes for gallium recovery. University of Maryland students and Center for Analytical Chemistry scientists have collaborated with us in isolating and characterizing the siderophore structure and studying iron and gallium binding phenomena by NMR. We have been invited to discuss these macroligand and other of our metal bioaccumulation studies at the 1989 International Symposium on Metallurgical Processes for the Year 2000 and Beyond.

A joint program with Montana State University, funded by the Strategic Highway Research Program, investigates the chemical and physical structure of asphaltic cements, in particular the time and temperature dependence of molecular aggregation. Solution and solid state nuclear magnetic resonance techniques are used in this work.

A joint NIST-Colorado State University project on molecular composites has been started as part of a large DARPA program. The main thrust in this project is to determine whether the rigid rod molecules that form the bases for a molecular composite are dispersed on a molecular level in the matrix composed of flexible chains. It is believed that maximum mechanical properties can be achieved with this optimum dispersion. Prof. J. K. Stille of Colorado State University is providing the materials, and NBS is developing the methodology for characterizating the degree of dispersion.

A joint program with Drs. Ron Eby and Herzl Chai of Johns Hopkins University is investigating the use of adhesive joint fracture tests as a method to simulate, in a controlled way, interlaminar fracture in a composite. Johns Hopkins is performing the fracture experiments while NIST is supplying expertise in the analysis of crack-tip deformation zone effects when the zone is constrained in a thin bond line or a composite. The work could lead to a new fracture test with important advantages over tests performed with composites.

The failure behavior of toughened adhesives is the subject of cooperative work with Dr. A. J. Kinloch of Imperial College (London) and Dr. S. S. Wang of the University of Illinois. The program is experimentally characterizing the growth of the crack-tip deformation zone during loading and comparing the results with predictions from finite element models. Such studies are a first step in developing failure criteria for these systems.

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.

Studies on the development of residual and transient stress in dental glass coated metal stress are being pursued jointly with Tokushima University, Japan and a manuscript on the effects of various elements on the casting of dental alloys has been co-authored with a researcher from Tokyo Medical and Dental University. Group members also serve on study sections for grants from the National Institute of Dental Research and the National Cancer Institute. Two members serve as consultants to the U. S. Navy. A collaborative study with Loyola University on fluoride caries inhibition is underway. guest Scientists from the Rudjer Boskovic (Yugoslavia) and Nihon University (Japan) have been working on calcium phosphate chemistry Calcium phosphate cements are being developed cooperatively with scientists at Taiwan University. Collaborative work with a University of Maryland researcher is in progress on statistical methods to predict results of clinical studies in progress and plasma sterilization of instruments is being pursued with the U. S. Navy.

Associated Activities

Invited Talks

Division personnel presented a total of 88 invited talks on research activities at the following types of organizations and symposia: industrial laboratories, 12; international symposia, 14; universities, 27; topical symposia, 10; national and government laboratories, 5; professional society meetings, 17; and Gordon Conferences, 4.

SRMS

Certificates have been issued for two polyethylene SRMS (1496 and 1497) which are similar in composition to polyethylene resins used in natural gas distribution systems. These SRMS are expected to facilitate test method development, standardization of test methods, and interlaboratory comparisons of test data.

Certification of SRMS, n-t-butyl 2-benzothiazole sulfenamide, a rubber compounding SRM, was completed. The rubber industry uses rubber compounding SRMS in ASTM test protocols for qualifying rubber materials.

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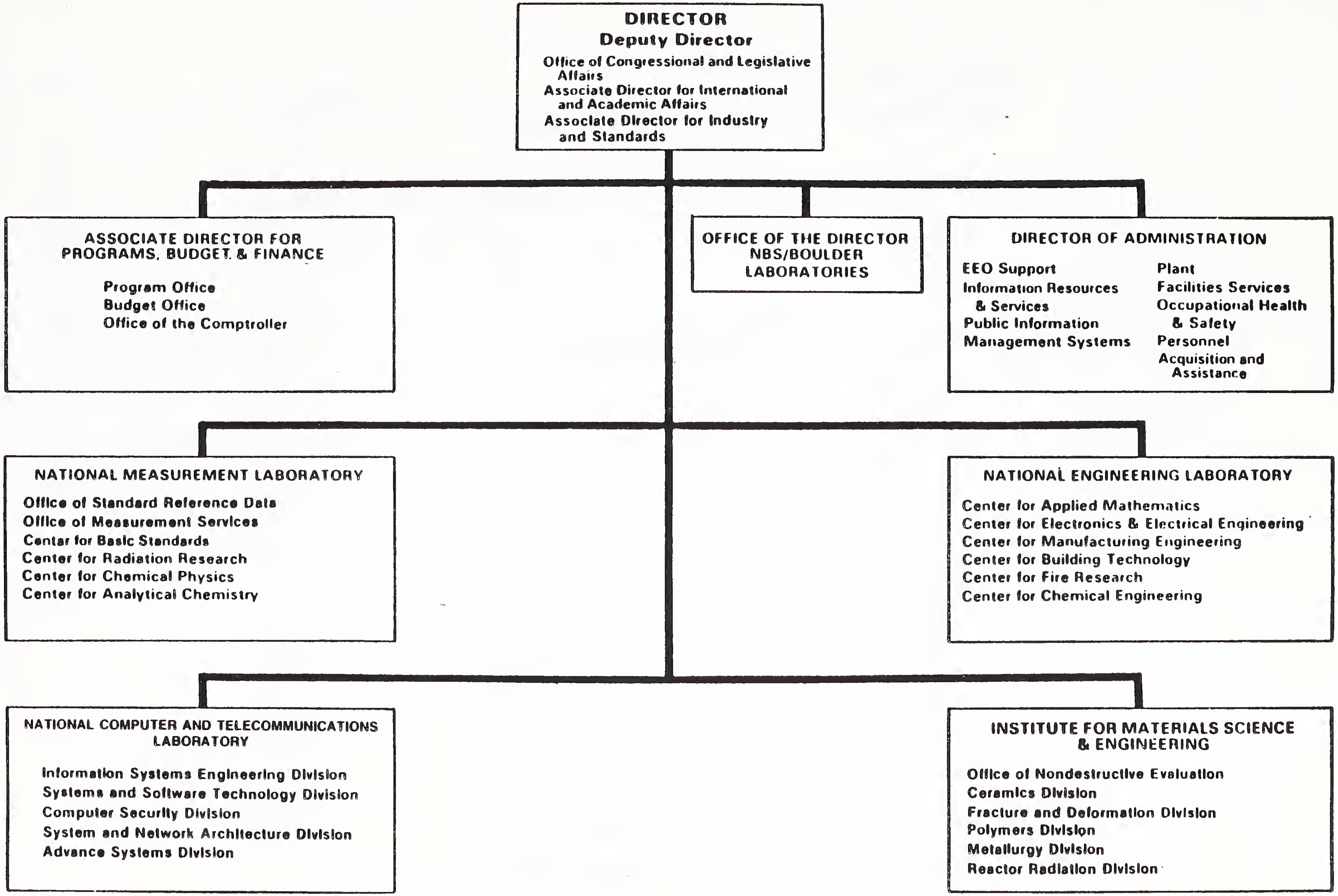

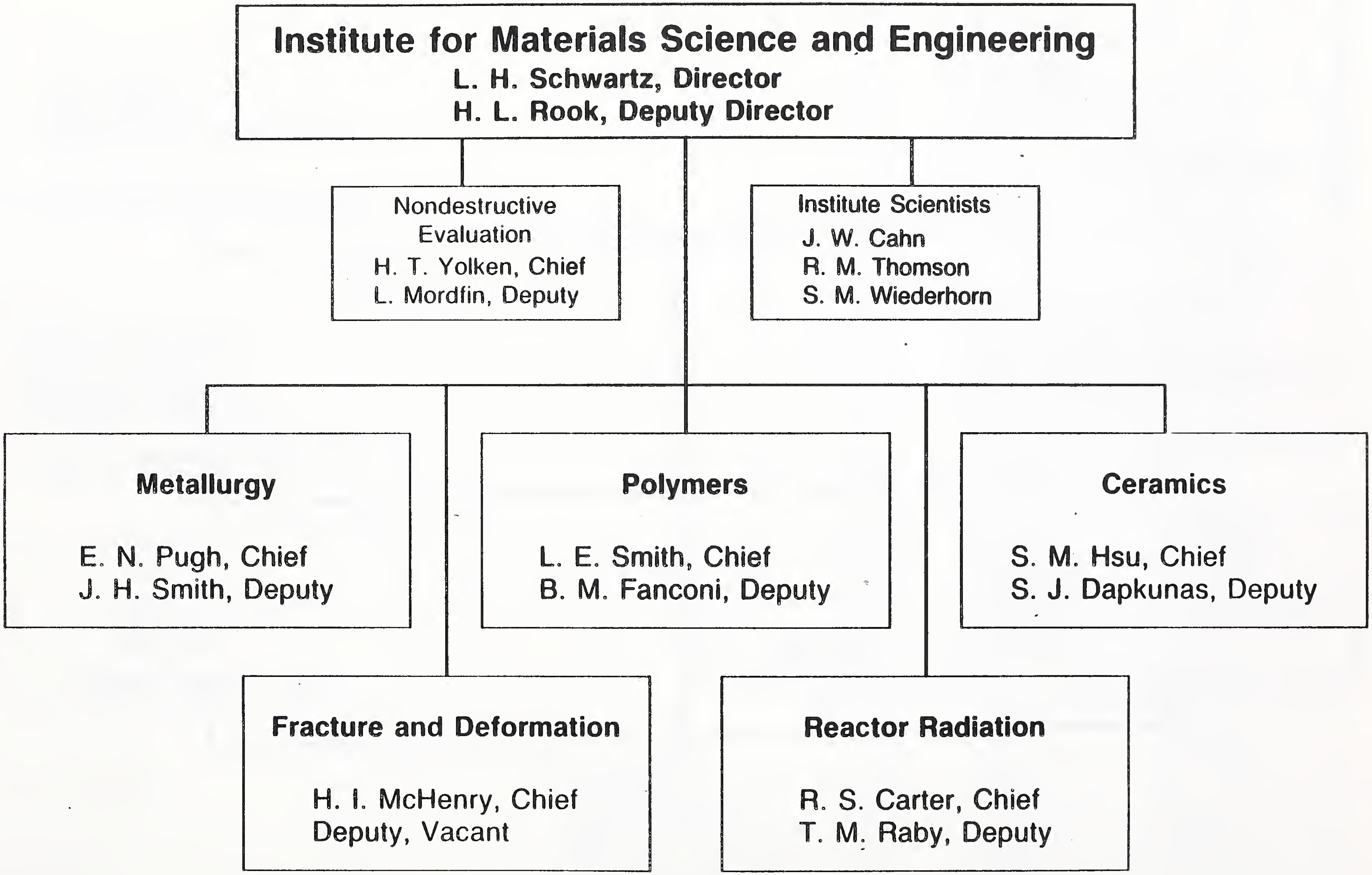

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10. SUPPLEMENTARY NOTES

☐ 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 88 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)*

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