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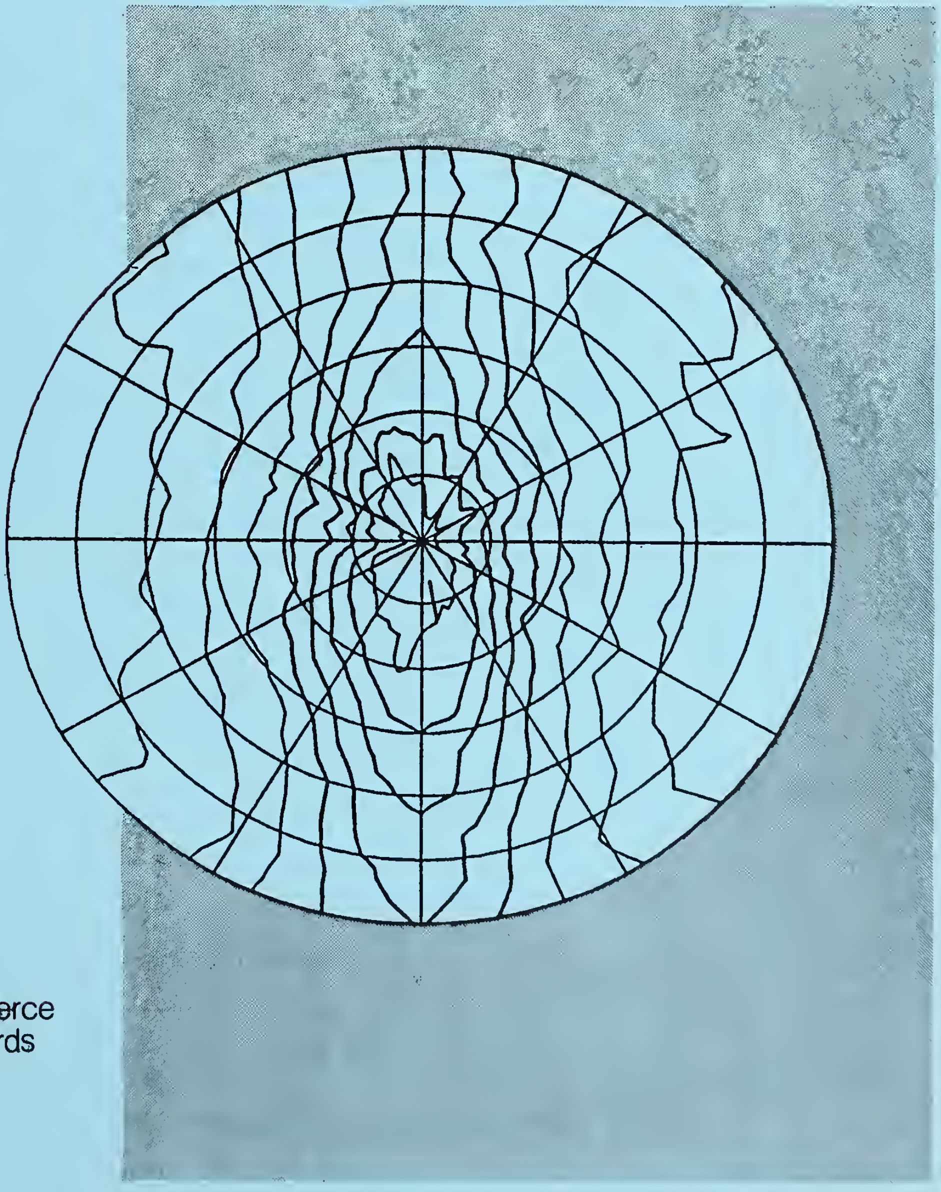

NAS-NRC
Assessment Panel
January 20-21, 1987

NBSIR 86-3437
U.S. Department of Commerce
National Bureau of Standards

Technical Activities 1986

X-ray pole figure diagram of the 200 reflection from an oriented polyethylene film. The figure was taken on a highly automated x-ray apparatus recently constructed at NBS that is available to industrial and academic users.

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

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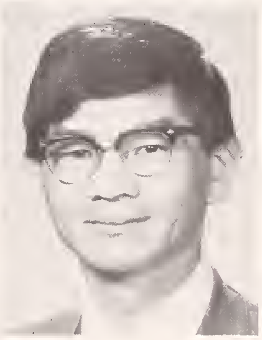

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INTRODUCTION

POLYMERS DIVISION

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

The Polymers Division is responsible for providing standards, measurements, and fundamental concepts of polymer science to assist U.S. industries that produce, process, or use polymers as an essential part of their business. Plastics, elastomers, and synthetic fibers now form the basis of industries that add over $100 billion of value by manufacture to the U.S. economy and these industries are growing rapidly relative to other basic materials industries. This growth rate is due primarily to the extreme versatility of synthetic polymers, whose wide range of possible properties offer opportunities for scientists to create innovative materials for nearly any new product. The polymer industry has vigorously pursued these opportunities and continues to introduce new polymers, process methods, and applications at a high rate. Examples of these new applications include trends for the increased use of polymers in packaging, construction, transportation, national security, dentistry, and medicine. The Division's programs are structured to deliver outputs that meet current needs as well as prepare for the changing needs of the industry over the next decade.

The organization of the Division consists of three property-oriented Groups and three material-oriented ones. The Groups concerned with electrical, chemical, and mechanical performance of polymers concentrate on the relationship of polymer structure to properties and especially on the measurement of the response of polymers to electrical, chemical, or mechanical stress. The programs of these Groups focus on the use of fundamental science to provide standards, measurement methods, and solutions to technological problems.

The Polymer Blends Group is responsible for providing fundamental data and concepts related to the development and processing of blends. Polymer blends are one effective way for domestic polymer producers to respond to competitive pressure from foreign producers with access to very inexpensive feedstocks. New products can be tailored to meet specific market requirements by blending two or more polymers, without abandoning present production facilities and without the large capital expenditures necessary to produce a totally new polymer. The principal industrial need in this field is for a fundamental science base to underlie the design and processing of new blends. This incudes needs for measurement methods to produce data for polymer phase diagrams, measurement methods and data on the microstructure of phase-separated blends, data on polymer diffusion and the kinetics of phase separation, and theoretical models that accurately describe the thermodynamics and kinetics of blends.

Although only about 10% of polymer production is now used in polymer matrix composites, the current and potential impact of these materials on other industries is dramatic. Military and aerospace uses of advanced composites are already large and diverse, amounting to about 40% of all advanced polymer composites. In the next ten years, advanced composites are predicted to have an annual value of over $10 billion and many other markets in the civilian sector will certainly expand. By the year 2000, the automotive industry may well be the largest single market for polymer composites with potential applications in structural components of the frame and suspension as well as in body panels. Many other opportunities exist in the construction, machinery, and electronics markets.

Two major factors have inhibited the growth of composites in these mass markets: inability to process the materials inexpensively and reliably; and uncertainty about the performance of these anisotropic materials under complex loads, particularly at failure. The Composites Group has programs aimed at solving some of the measurement and basic science aspects of these two problems. More efficient processing will come from automated manufacture aided by appropriate feedback control sensors. The identification of materials properties that can be monitored and development of measurement methods suitable for process control are major objectives of the Group with additional support from the NBS Non-Destructive Evaluation program.

Failure behavior of composites is very complex and the fundamental science of heterogeneous materials is not advanced enough to be confident of predictions based on much less than prototype testing. Important new work has focused on a fundamental understanding of the structure of crosslinked epoxy networks and measuring the response of these networks to deformation. Small angle neutron scattering has been vitally useful to these studies and the results are illustrative of the kind of leap forward in understanding that is made possible by this NBS facility.

The Dental and Medical Materials Group is a model of effective private sector-government cooperation. For over sixty years the American Dental Association (ADA) and NBS have worked together to improve dental materials and devices. Virtually all the major materials used by dentists in the United States today have been developed or influenced by this joint program which includes the National Institutes of Dental Research, and foreign guest workers in the most comprehensive program of its kind anywhere in the world.

Each of these programs is described in more detail in this report. The report is organized into the six Groups as follows:

ELECTRICAL PROPERTIES
POLYMER STANDARDS AND CHEMICAL PERFORMANCE
MECHANICAL PERFORMANCE OF POLYMERS
PROCESSING AND RELIABILITY OF POLYMER COMPOSITES
POLYMER BLENDS
DENTAL AND MEDICAL MATERIALS

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

- An interpenetrating network of low molecular weight poly(ethylene oxide) containing dissolved salts and an epoxy resin has been demonstrated to perform well as a solid electrolyte. The dissolved salt forms mobile cross-links within the normally liquid PEO and apparently prevents it from phase-separating (pg. 5).

- A synthetic phantom which has the same dielectric heating characteristics as living tissue has been designed for the Food and Drug Administration. Organic salts are dissolved in an ethylene carbonate-propylene carbonate mixture and thickened with fumed silica or by cross-linking a methacrylate- terminated polyethylene glycol. Interfacial polarization is simulated by incorporating 1.5 μm-thick flakes of poly(ethylene terephthalate) (pg. 5).

- A series of three poly(methyl methacrylate) Standard Reference Materials are being produced with support from the Navy and the Office of Standard Reference Materials. These SRM's will be used for quality control of antifouling paints and as calibrating materials for the analysis of acrylic polymers. For SRM 1489, the highest molecular weight polymer in the series, a certificate has been issued certifying both the limiting viscosity number and the number-average molecular weight. The number average molecular weight of SRM 1488 with intermediate molecular weight has also been determined (pg. 10).

- Two linear low density polyethylenes used in gas piping (one with, and the other without pigment) have been characterized for certification as Standard Reference Materials, with support from the Gas Research Institute and the Office of Standard Reference Materials. Such standards will be useful not only to the gas distribution and associated industries but also to the rest of the scientific community (pgs. 24,32).

- A novel method, called Fluorescence Recovery After Photobleaching, has been applied to rapidly determine the diffusion coefficients of polymers in solutions. The diffusion of a polystyrene in dilute and semi-dilute solution has been measured over a concentration range from 0.02 g/ml to 0.3 g/ml. In the low-concentration regime the diffusion coefficient has been found to be inversely proportional to the one-half power of polymer concentration, and in the semi-dilute regime, the seven-fourth power of concentration. These results agree well with a recent theory (pg. 13).

- A nuclear magnetic resonance technique has been developed and applied to determine the partitioning of chain ends and branches between the crystalline and non-crystalline regions of polyethylenes. Side groups (branches) in polymers can greatly affect mechanical properties and performance. A major problem in predicting such effects is that branches may be concentrated in regions of crystalline polymers (p. 22).

- The molecular mechanism for large strain deformations in epoxies has been shown by neutron scattering experiments to be at variance with current knowledge concerning the deformation mechanisms in rubbers, and other cross-linked polymers. In epoxies cured with short chain amines the average distance between crosslinks in the molecular network stays unchanged even when the macroscopic strain reaches values up to 30%. This result suggests that the deformation mechanism is either defect controlled or unfolding of the network (pg. 42).

- Viscosity changes during cure have been correlated in model materials with the results from four measurement techniques that have on-line potential: ultrasonics, fluorescence, photo-bleaching, and dielectrics. Both similarities and differences have been highlighted as a critical first step toward evaluating the potential of these measurement methods. Proper control of viscosity is the single most important factor in efficient composite processing (pg. 35).

- The molecular weight dependence of the binary interaction parameter, χ, has been obtained for polystyrene/poly(vinylmethylether) blends using small angle neutron scattering. This has been used in conjunction with a temperature jump light scattering technique to obtain the mutual diffusion coefficient of this polymer blend system above and below the critical point. The critical slowing down, and the analytical continuity of free energy and diffusivity have been demonstrated quantitatively for the first time (pg. 50).

- Blends of poly(vinylidene fluoride) (PVF_2) and poly(ethylacrylate) have been used in their compatible region to study the crystallization process and morphology of PVF_2. The structures formed evolve from single crystal lamellae to more complex aggregates and eventually to spherulites. The morphology has been studied as a function of PVF_2 concentration (pg. 51).

- Flexible prepolymer monomers and bulky diluent monomers (based on vinyl thermosetting silyl ethers) were synthesized that yield high filler content dental composites with reduced water uptake, adequate mechanical strength, and excellent esthetics (pg. 57).

- The susceptibility of glass ionomer cements to brittle fracture and degradation under acidic conditions has been reduced by the incorporation of water-soluble or water compatible vinyl resin systems (pg. 57).

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Stansbury, Jeffrey W.	• Synthetic chemistry • Polymers and polymer composites • Polymerization expanding monomers
Takagi, Shozo*	• Crystallography • X-ray diffraction • Calcium phosphate compounds
Tesk, John A.	• Casting of alloys • Strength of dental systems • Thermal expansion & properties of dental materials • Finite element studies • Porcelain-metal system
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Zapas, Louis J.	● Continuum mechanics & Rheology ● Non-linear mechanical behavior of polymers ● Static fatigue of plastics ● Finite elasticity (rubbers)

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ELECTRICAL PROPERTIES

The goal of the task on electrical properties is to carry out long-range research involving the interaction of electric fields with polymers. Such research provides the basis for new or improved measurements which will lead to higher performance of polymers in existing applications or to entirely new applications. The program includes research on high voltage insulation, ionic conduction, piezoelectricity, pyroelectricity, and electro-optic phenomena. Results in the form of data, measurement techniques, and scientific concepts are communicated to funding organizations in the form of technical reports. In most cases, the results are also published in archival journals, presented orally at scientific meetings, discussed with visitors, and shared with research associates who come to work with us. In some cases, the research results in a measurement system which is delivered to the sponsor.

The measurement of dielectric constant and dielectric loss as a function of frequency and temperature has long been used to probe the molecular motions in polymers. Development of a time domain dielectric spectrometer at NBS has extended the ability of these measurements to follow dielectric properties which evolve with time, since data for a wide frequency range can be obtained in an interval of time comparable to the reciprocal of the minimum frequency of interest. Also, an automated system which measures dielectric constant and loss at a series of fixed frequencies between 100 Hz and 10^9 Hz is being used to infer DC conductivity of polymer systems where polarization becomes a problem.

A thermal pulse technique which has proven useful for measuring polarization as a function of position across a thin film of polymer has been improved to increase sensitivity and resolution so that the distribution of charge can now be measured. The role of trapped charge, leading to locally high electric fields, is being examined for its effect on dielectric breakdown in cable insulation.

Examples of new electric applications of polymers are piezoelectrics, pyroelectrics, solid electrolytes, and electro-optics. NBS has made significant contributions to the understanding of the mechanisms responsible for piezoelectric and pyroelectric properties of polymers. Details of these models are being refined and transducers using polymer piezoelectrics are being developed for specific applications. Research continues on the dissolution of salts and the transport of ions in polymers such as polyethylene oxide and linear polyethylene imine. Of particular interest is the diffusion of Li^+ as determined by neutron depth profiling. The concept of an interpenetrating network for ionic conduction has been reduced to practice by employing a low molecular weight PEO and an epoxy resin. A new effort within the group is directed toward the synthesis and evaluation of new polymers for electro-optical properties.

FY 86 Significant Accomplishments

- The sensitivity and resolution of space charge distribution in polymer films using the thermal pulse technique has been greatly improved by using a dye laser to provide a short pulse of intense heat.

- A synthetic phantom which has the same dielectric heating characteristics as living tissue has been designed for the Food and Drug Administration. Organic salts are dissolved in an ethylene carbonate-propylene carbonate mixture and thickened with fumed silica or by cross-linking a methacrylate- terminated polyethylene glycol. Interfacial polarization is simulated by incorporating 1.5 μm-thick flakes of poly(ethylene terephthalate).

- An interpenetrating network of low molecular weight poly(ethylene oxide) containing dissolved salts and an epoxy resin has been demonstrated to perform well as a solid electrolyte. The dissolved salt forms mobile cross-links within the normally liquid PEO and apparently prevents it from phase-separating.

Automated Dielectric Measurements

F. I. Mopsik

The recent development of a time-domain dielectric spectrometer has continued to receive attention. This instrument measures the charge response of a dielectric to an applied voltage step for times from 10 μs to 3000 s and transforms the data into the frequency domain for frequencies from .0001 Hz to 10 kHz. A commercial version of the instrument is actively being developed by IMASS, Inc., Hingham, MA through the Research Associate program at NBS and is nearing completion. A further development has been the signing of a Research Associate agreement by GE Research Laboratory in Schenectady, NY to facilitate transfer of a copy of the instrument for use in their laboratory.

The instrument's sensitivity, accuracy and frequency range has allowed it not only to be used in relaxation studies on PVDF and the study of epoxy resin cure but in routine relaxation time studies on other polymers as background information for other work. Measurements have been made on polycarbonate, SURLYN and ULTEM to clarify their behavior.

Cure Monitoring in Epoxy Resin Systems

The development of the dielectric spectrometer and an A-C conductivity system has allowed an intensive study into the use of dielectric measurements for monitoring the cure of epoxy resins. Several different resins cured with imidazole showed that a 50 Hz conductance measurement can readily follow the curing reaction of the resin system. Cross comparisons were made with measurements of viscosity, ultrasonic elastic constant, and exotherm on common samples. These studies demonstrated that the conductance could follow the curing reaction into the final state at least as well as the other techniques. Furthermore, the conductance data was not simply related to viscosity and could show features, such as an initial ion-forming reaction, that were not readily apparent in other measurements. Also, controlled studies on mixed resin aged at room temperature demonstrated that a conductance measurement could be used to monitor the state of mixed resin systems quite readily. This could prove of great value in establishing cure cycles a priori and the suitability for use of mixed resin.

Preliminary measurements were made on an epoxy-diamine system. This system had a much lower initial conductance and, for the first time, evidence of dipolar relaxation was seen. This was indicated by the appearance of a conductance maximum toward the end of the cure reaction. Measurements with the dielectric spectrometer were typical of a relaxation process. These measurements were also useful in showing the limitations in interpreting the data due to sample evolution on a time scale approaching the measurement frequency. With the development of a new, faster changing temperature control system, this work will be continued and cross-compared with other measurement methods. Also, measurements on higher temperature, commercial resin systems will be made.

Piezoelectric Polymers

S. C. Roth, A. J. Bur, and M. G. Broadhurst

The development of piezoelectric polymer gauges with a protective layer of polyetherimide has been concluded with the delivery of 15 calibrated gauges to Eglin AFB. The inert layer of glassy polymer protects the piezoelectric polyvinylidene fluoride from damage when imbedded in soil containing sharp particles and delays the temperature rise due to adiabatic heating when used to measure pressure changes in air. Complications arise for times longer than about 2 ms which are believed to be associated with mechanical relaxation in the protective layers.

Another research project is directed toward measurement of piezoelectric response to shear in piezoelectrically active polymers and development of methods to enhance such response for specific transducers. According to current models in which molecular dipoles are aligned preferentially normal to the electrode surface of polymer thin films, shear stresses are expected to produce negligible charge response at the electroded surface. If dipoles could be aligned parallel to the electroded surface, shear response is expected to be much larger. Attempts to align dipoles in an electric field parallel to the surface have been unsuccessful and the present approach involves poling thick films of polymer and then slicing and depositing electrodes on what were the edges of the specimen.

A cooperative mean-field model has been analyzed for pyroelectric properties. The model assumes that the orientation of independent molecular chain segments in the crystalline phase of PVDF and its ferroelectric copolymers can be determined from a six-site rotational potential energy function where the energy of a site is linear with occupation probability. The potential function is chosen to give the infrared-observed vibrational frequency of 70 cm^{-1}, and a barrier height of about 12 kT suggested by dielectric relaxation rates. A six-fold cosine function meets both with requirements. Analytical solutions for the case of no applied electric field yield a first order ferroelectric transition. The remanant polarization and disorder contribution to the pyroelectric coefficient were calculated for the ferroelectric phase. The model predicts that for PVDF more than half of the pyroelectric response is secondary and due to thermal expansion in the thickness direction while changes in the order parameter with temperature make up the remainder. Surprisingly, the primary response occurs much later (milliseconds) than the secondary response (microsecond) because the dipolar reorientation accompanying the disorder process involves rotation over large (∿12 kT) energy barriers. This result seems quite consistent with existing data and offers a satisfactory alternative to the popular reversible crystallization theory of pyroelectricity in PVDF.

Thermal Pulse Measurement of Space Charge

A. S. DeReggi

The measurement of the distribution of space charge across the thickness of dielectrics has been advanced by replacing the flash lamp which served as a thermal pulse source by a pulsed dye laser. The dye laser can deliver thermal pulses with shorter duration (∿1 μs vs 50 μs before) and higher power (up to 1 MW vs ∿30 kW before). Evaporation of the electrodes on the sample now limits the energy per pulse rather than the output capability of the source itself.

The shorter pulse duration has increased the spatial resolution of the measurements. Prior measurements on polyvinylidene fluoride (PVF_2) poled at room temperature had shown that ferroelectric switching occurred more readily in the central parts of a sample than near the surfaces, although it appeared, within the resolution then available, that finite polarization extended to the surfaces. New measurements with increased resolution show now that the polarization in similar samples falls to essentially zero within ∿1 μm of the surfaces. The inhibition of switching near the surfaces is not understood presently although electrode constraints could be an explanation. Ferroelectric switching is believed to occur through a 60° dipole rotation accompanied by a displacive transformation of the unit cell of the polar crystal phase. The displacement requires an extension of the unit cell by nearly 2% in a direction perpendicular to a face diagonal. Any restriction on this displacement could prevent poling.

During this FY, space charge measurements in new dielectrics for electric power cable insulation have continued under the sponsorship of the Electric Power Research Institute. The NBS task is to gain an understanding of charging phenomena and the kinetics controlling its distribution. These factors affect the internal electric fields and their distribution, and hence are thought to affect long term aging behavior and dielectric failure. Furthermore, identification of materials with tendencies to accumulate charge of opposite signs might help guide the development of compatible blends of these materials which might remain electrically neutral. In a coordinated effort also involving a research team at the U. of Connecticut, the blend polyethylene and a Zn-ionomer Surlyn™ has been investigated. The U. of Connecticut team prepared samples one composition (80% PE) and performed thermally stimulated current studies, while NBS was responsible for space charge measurements and theoretical modeling. In the initial stages of this work, the effects of charging voltage, charging temperature, charging time and electrode materials were investigated. Space charge measurements showed dependence on the variables cited, but many of the observed effects were judged to depend on the sample history. The procedure of annealing samples was not appropriate for the blend due to phase separation. Studies on annealed Surlyn samples were carried out with charging voltages of up to 800 V/mil and charging temperatures of room temperature and of 60 °C, the nominal allowed operating temperature of power cables. The charging behavior for short charging times (up to tens of minutes) was found to vary among samples, which showed hetero charge in some cases and homocharge in other cases. However, for long charging times (hours or days) all Surlyn samples exhibited similar behavior in that they showed accumulation of charge of negative sign with a nearly uniform accumulated charge distribution. Even samples which showed heterocharge initially (those charged for short-to-intermediate time intervals), exhibited a nearly uniform negative charge distribution after aging times of several days at room temperature. The samples studied had very high resistivities between room temperature and 60 °C. Estimates of the Maxwell relaxation time at 60 °C give a few hours. It is reasoned, therefore, that the Maxwell relaxation time is a natural parameter separating the different charging behavior at long and short times. Furthermore, given enough time, all samples achieve the same charge equilibrium state.

Polymer Dielectric Phantoms

M. G. Broadhurst, C. K. Chiang, and G. T. Davis

A synthetic phantom has been designed which has the same dielectric heating characteristics as living tissue so that testing can be done using it rather than live subjects. This material is needed by the Food and Drug Administration (FDA) and biomedical instrument makers for testing and calibrating devices that subject human tissue to high-frequency electromagnetic radiation.

The FDA's Center for Devices and Radiological Health asked NBS to help design a more stable material than the presently used aqueous biopolymer-based phantoms. The synthetic phantom is a mixture of four components, chosen to provide the same electrical properties as the corresponding components in live muscle. These components are: 1) ethylene and propylene carbonate, organic solvents with dielectric constants similar to water; 2) tetraethylammonium tetrafluoroborate, an organic salt to provide conductivity similar to biological electrolytes; 3) 1.5-micrometer-thick poly(ethylene terephthalate) flakes to provide interfacial polarization similar to that found at cell walls; and 4) fumed silica, a thickening agent to provide mechanical stability. The resulting composite is more stable to drying and biological attack and can be used over a wider frequency range than existing phantoms. It also has a lower heat capacity and thermal diffusivity that should improve the sensitivity of temperature distribution measurements inside the material during electromagnetic heating experiments.

Ionic Conduction In Polymers

B. J. Bauer, C. K. Chiang, R. M. Briber, and G. T. Davis

A new type of polymeric electrolyte has been developed based on interpenetrating polymer networks (IPNs). Polymeric films that have high ionic conductivity have many applications such as in all polymeric batteries. The conductivity of salt-polymer systems is limited by the glass transition temperature of the polymers. Low molecular weight polymers such as polyethylene oxide (PEO) have higher conductivities, but they are liquids that cannot form films.

IPNs have been synthesized that have two co-continuous phases. One is a cross-linked epoxy phase that provides strength and dimensional stability. The other phase is a low molecular weight PEO (MW = 400) with dissolved salt which gives high conductivity (as high as 10^{-4} S/cm). This is an order of magnitude better than previous one-phase films.

Transmission electron microscopy shows a two phase structure with the size scale ranging from 0.1 to 0.5 microns. The conductivity of the films is constant up to 35% (by wt.) epoxy and then drops exponentially. The optimum mechanical and electrical properties come around 35% epoxy. Films made with cross-linked poly(methyl methacrylate) as the support phase have similar properties. A patent is pending on these polymeric electrolytes.

As part of our program on solid electrolytes, preliminary measurements of the diffusion coefficient of Li^+ in poly(ethylene oxide) have been performed using neutron depth profiling in cooperation with personnel from the Center for Analytical Chemistry at the NBS reactor. The technique is based upon the nuclear reaction in which a lithium 6 nucleus captures a neutron and decays immediately to yield a triton particle and an alpha particle, each of known energy. Energy of each particle is dissipated as a known function of distance in the polymer medium. A measurement of the number of particles as a function of energy can be converted to concentration of ^6Li as a function of depth within the polymer - up to about 50 μm from the surface closest to the detector. The initial experiments involved pressing a 100 μm - thick film of PEO against a thick film of PEO containing 10 mole percent of $LiClO_4$ and following the appearance of Li in the thin film by counting the emerging α and T particles in increments of 30 minutes over a period of 20 hours. The concentration of Li in the thin film was then measured much less frequently over the next four weeks. From a time-lag analysis, the diffusion coefficient of Li in the "pure" PEO was found to be 4×10^{-9} cm^2/sec. The equilibrium concentration of Li implies that the salt is entirely in the non-crystalline regions and that crystallinity is not reduced if maintained at room temperature.

Liquid Crystalline Polydiacetylenes for Non-Linear Optics

M. A. Schen

For optical based telecommunications and signal processing, a strong need exists for non-linear optical materials which can be fabricated into switching, logic, and phase conjugated devices. Currently, for example, second and third order phenomena are being exploited for frequency doubling and tripling using ceramic semiconductors such as GaAs and $LiNbO_3$. It is now evident, though, that organic compounds containing π-electron systems can offer intrinsic non-linear susceptibilities $\chi^{(n>1)}$ exceeding those of known inorganic structures. Specifically, polydiacetylenes (PDA) have been shown to exhibit exceptionally large $\chi^{(3)}$, picosecond scale response times, phase matching, high laser damage threshold energies, and optical transparency throughout much of the visible and near infra-red regions. These factors are responsible for making PDA a likely candidate for future devices.

Nearly all disubstituted diacetylene monomers, once polymerized, form insoluble, unprocessable polymers. For this reason, many optical studies have been performed on as-polymerized single crystals or organized Langmuir-Blodgett multilayers. Examples of soluble PDA's do exist, such as 1,4-tetramethylene butoxycarbonylmethylurethane diacetylene (4BCMU) and1,4-tetramethylene-p-toluenesulfonate diacetylene (PTS-12). During reprecipitation of 4BCMU from solution, inter-side chain hydrogen bonding introduces side chain organization which in turn influences backbone conformational order and gelation occurs. Gelation has not been observed in PTS-12.

The objective of this research is to prepare a new class of disubstituted diacetylene monomers which, after solid state polymerization, will be soluble, processable, and exhibit liquid crystalline (LC) behavior in the bulk. In essence, a new level of side chain molecular ordering will be introduced into PDA compositions. This will be accomplished by preparing side chain LC architectures analogous to the methacrylate based LC polymers explored by Ringsdorf et al.

POLYMER STANDARDS AND CHEMICAL PERFORMANCE

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

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

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

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

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

FY 86 Significant Accomplishments

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

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

- A novel method, called Fluorescence Recovery After Photobleaching, has been applied to rapidly determine the diffusion coefficients of polymers in solutions. The diffusion of a polystyrene in dilute and semi-dilute solution has been measured over a concentration range from 0.02 g/ml to 0.3 g/ml. In the low-concentration regime the diffusion coefficient has been found to be inversely proportional to the one-half power of polymer concentration, and in the semi-dilute regime, the seven-fourth power of concentration. These results agree well with a recent theory.

- The diffusion coefficients of two fluorescent dyes in polystyrene solutions have been measured over a wide concentration range by the technique of fluorescence recovery after photobleaching. In all cases, the diffusion coefficient decreases with polymer concentration more slowly when the molecular weight is 18,000 than when the molecular weight is 110,000 or 500,000.

- Changes in fluorescence spectra occur during the formation of polyimide polymers from poly(amide-acid). These changes can be measured in-situ and non-destructively to monitor the course of imidization.

Standard Reference Materials and Data

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

Work in this subtask proceeds primarily along two lines: Production of polymer standards; Critical evaluation of experimental data on polymers. The linear low density polyethylene standards currently under development, which are partly supported by the Gas Research Institute, will aid in the development of polyethylene gas pipes with improved properties. The poly(methyl methacrylate) standards currently in production will aid the Navy, which is partially supporting their production, in the development of long-lived antifouling paints for ships' hulls. In addition, both kinds of standards will be generally useful in the plastics and related industries, both for equipment calibration and as materials for research. The critical evaluation of literature data on the relationships between limiting viscosity number and molecular weight for atactic polystyrenes will aid in materials characterization in this important segment of the plastics industry. Development of a self-calibrating gel permeating chromatograph should eventually result in substantial reductions in the cost of producing polymer Standard Reference Materials, and should allow much more detailed characterization of polymeric materials than has thus far been practical.

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 would be useful to the rest of the scientific community because there is a growing need for higher molecular weight polyethylene standards.

The melt flow rate, a widely used measure of polymer processing properties, has been measured for SRM 1497 by ASTM method D1238-82 under three standard test conditions. The value obtained under one of these, called the melt index condition, will be certified. The other two melt flow rates will be given as supplemental information. Studies preliminary to the certification of the limiting viscosity number of SRM 1496 in 1,2,4-trichlorobenzene at 130 °C are under way. Future plans include estimation of the distribution in molecular weight of both materials by gel permeation chromatography as supplemental information, and measurement of a molecular weight of SRM 1496 for certification.

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 blended and bottled. They have been examined by NMR to check chemical identity and tacticity. The uniformity of the materials has been checked by capillary viscometry measurements.

Capillary viscometry measurements have been used to determine the limiting viscosity number (intrinsic viscosity) of SRM 1489 in toluene at 25 °C. The number average molecular weight has also been determined by membrane osmometry in toluene at 25 °C for both SRM 1488 and 1489. A certificate has been issued for SRM 1489 certifying both the limiting viscosity number and the number average molecular weight.

Revalidation of Polyethylene Standard Reference Materials

For a variety of reasons, it was deemed desirable to have a measure of assurance that the materials presently available for sale as three of our polyethylene Standard Reference Materials (SRM's) have not changed significantly since their original certification. Accordingly, we have measured melt-flow rate and limiting viscosity number under the same conditions as those used for the original certification of SRM 1475 Linear Polyethylene (Whole Polymer) and SRM 1476 Branched Polyethylene (Whole Polymer). For both properties and both SRM's, the differences between the values measured now and those originally certified are too small to provide significant evidence for any change in these materials. A similar comparison, using only limiting viscosity number, will be carried out for SRM 1482 Linear Polyethylene (Narrow Molecular Weight Distribution).

Critical Evaluation of Mark-Houwink Constants for Poly(methyl methacrylate)

One of the most important physical properties of a polymer is its average molecular weight, which largely determines processibility and performance properties. Since absolute determinations of molecular weight are time consuming and are not made routinely, relative methods, such as solution viscosity and size exclusion chromatography (also called gel permeation chromatography) are used instead.`

The limiting viscosity number (intrinsic viscosity), $[\eta]$, and the molecular weight, M, are related, empirically, by a simple power law:

$$[\eta] = KM^a$$

where K and a are the empirically determined Mark-Houwink parameters, which depend on the specific solvent and temperature. An incomplete compilation of these data can be found in the handbooks, but a critical assessment is not yet available. Yet these data are used extensively to obtain molecular weights as well as to calibrate size exclusion chromatography columns. Detailed examination of the literature revealed that many of the determinations of K and a were made by indirect rather than by absolute measurements of molecular weight, or by the use of whole polymers rather than fractions, leading to large uncertainties. Determinations such as these were rejected in favor of direct determinations of molecular weight by absolute methods such as light scattering or osmotic pressure.

Review papers for linear polyethylene and atactic polystyrene have been published previously. This past year the literature for poly(methyl methacrylate) has been critically examined and the K and a values for a variety of solvents used for viscosity and size exclusion chromatography measurements have been recommended. These are acetone, benzene, chloroform 2-butanone, and tetrahydrofuran, as well as for some less frequently used solvents. The values for the coefficient K in the relation $[\eta] = KM^{0.5}$ for several theta solvents are also reported.

The results of this evaluation have been submitted for publication in the Journal of Physical and Chemical Reference Data.

Self-Calibrating Gel Permeation Chromatography

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

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

Sample preparation and filtering procedures have been developed which permit injection of calibrants directly into the light-scattering detector, bypassing the GPC columns.

Molecular Characterization

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

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Work in this subtask concerns the development of improved methods for characterizing polymeric materials, and the development of fundamental concepts related to the solution properties of polymers. Fluorescence measurements of polymer diffusion and polymer-polymer interactions will provide data that are needed for heat-joining of polymers, for designing polymerization reactors, and for producing molecularly reinforced composites. Since almost all polymers in use contain additives to maintain and enhance their useful properties, the experimental study of diffusion of small molecules in entangled polymers will provide the data needed for predicting the lifetimes of polymers containing additives. The theoretical studies of translational diffusion constants and chain-molecule dynamics will yield fundamental concepts that will not only guide the experimental work on polymer-solution properties but also give insight on the processibility and the end-use properties of polymeric materials. Finally, the fluorescence techniques developed for diffusion measurements and for characterizing the formation of polyimide polymers have been used to monitor in-situ the cure of epoxy resins and polyimide polymers as described elsewhere in the report.

Diffusion of Polymers in Semi-Dilute Solutions by Photobleaching Method

Verification of theories of self-diffusion and reptation in semi-dilute solutions has been hampered by the lack of a rapid method for determining the diffusion coefficient of polymers. We have applied a novel method, called Fluorescence Recovery After Photobleaching (FRAP), to rapidly measure the diffusion coefficient of a polystyrene polymer in semi-dilute solutions [1]. The measurements cover nearly two decades of concentration and also extend to the low-concentration regime. These results agree with a recent theory [2] which predicts that self-diffusion coefficient varies inversely with seven-fourths power of concentration in the semi-dilute regime, and varies inversely with the one-half power of concentration in the low-concentration regime. In collaboration with Prof. E. -S. Wu of the University of Maryland, Baltimore County, we are now using the FRAP method to measure the diffusion of polymers in both a theta and a good solvent, as a function of shape, concentration, and molecular weight.

1. F. W. Wang, R. E. Lowry, and E. -S. Wu, Polymer, 26, 241 (1985).
2. W. Hess, Macromolecules 19, 1395 (1986).

Translational Diffusion Measurements of a Conducting Polymer in the Melt

The unusually high ionic conductivity observed in polyethylene oxide (PEO) complexed with inorganic salts has stimulated considerable activity in the development of polymeric solid electrolytes. Fundamental questions concerning the specific interactions between PEO and the inorganic salts remain. We plan to investigate these specific interactions by measuring the translational diffusion coefficient of polymer complexed with salt in the melt. Diffusion measurements will be performed on our newly acquired fluorescence photobleaching apparatus. Narrow molecular weight distribution samples of fluorescently labeled PEO are prepared by our standard labeling method. The translational diffusion coefficients as a function of added salt, molecular weight of polymer, and temperature will be compared with existing conductivity data.

Diffusion of Small Molecules in Entangled Polymers

In collaboration with Professor E. -S. Wu of the University of Maryland (Baltimore County), we have used the technique of fluorescence recovery after photobleaching (FRAP) to measure the diffusion of fluorescent dyes in polystyrene solutions. The fluorescent dyes used are DiI-C6(3), 1,1'-dihexyl-3,3,3',3'-tetramethylindocarbocyanine perchlorate, and similarly structured DiIC1(3), which has two methyl groups instead of two hexyl groups. The large dynamic range of the FRAP technique together with the large viscosity of the solvent diethyl phthalate makes it possible to measure the diffusion coefficient over a wide concentration range, from 0.05 g/ml to 0.8 g/ml. The molecular weights of the polymers used are 17,500, 110,000, and 498,000.

We have found that, in all cases, the logarithm of the diffusion coefficient decreases linearly with the ratio of the volume of the polymer to the volume of the solvent. For both DiI-C1(3) and DiI-C6(3), the magnitude of the slope for 17.5 K polystyrene polymer is substantially smaller than those for 110 K and 498 K polystyrene polymers. For the latter two polymers, the slopes are the same within the experimental uncertainties. These results suggest that the characteristic volumes of DiI-C1(3) and DiI-C6(3) depend on whether the polymer forms an entangled network or not, and are greater in entangled solutions.

Translational Diffusion Constant Linear and Branched Chains

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

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

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

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

Characterization of Polyimide Polymers by Fluorescence Spectroscopy

Polyimide polymers are important in electronics and associated industries because they have properties suitable for photoresists and thermally stable insulators. We have used the fluorescence technique to monitor the formation of a polyimide polymer from 2,2-bis(4-phenoxyanilino)hexafluoropropane and a dianhydride like 3,3',4,4'-benzophenone-tetracarboxylic dianhydride (BTDA) or 2,2-bis(3',4'-dicarboxyphenyl)hexafluoropropane dianhydride (6F). Preliminary results show that the fluorescence spectrum of the poly(amide-acid) overlaps the spectra of the diamine and the dianhydride when the excitation wavelength is 355 nm. However, the formation of the polyimide polymer from the poly(amide-acid) is accompanied by red shifts in the excitation and the emission spectra. Therefore, the formation of the polyimide polymer can be monitored by measuring the increase in the fluorescence intensity at 550 nm when the sample is irradiated at 480 nm.

In collaboration with scientists from AT&T, we have initiated a project to monitor the formation of polyimide polymer from p-diaminobenzene and 3,4,3',4'-biphenyl-tetracarboxylic dianhydride. The formation of the polyimide polymer from the poly(amide-acid) is accompanied by red shifts in the excitation and emission spectra. Therefore, the formation of the polyimide polymer can be monitored by measuring the increase in the fluorescence intensity at 560 nm when the sample is irradiated at 460 nm.

Fluorescence Spectroscopy of Rod-like Polymers

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

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

We have measured the excitation and emission spectra of a dilute solution of poly(p-phenylene benzbisthiazole) (PBT) in methanesulfonic acid. We have also measured these spectra for a dilute methanesulfonic acid solution of 2,6-diphenylbenzo(1,2-d:4,5-d')bisthiazole (hereafter referred to as t-bisthiazole), a model compound of PBT. We have found that the emission spectrum of the PBT solution has its most intense band at 466 nm when the excitation wavelength is any of the following wavelengths: 270 nm, 320 nm, and 440 nm. The emission band for the PBT solution occurs at longer wavelength than the one for the t-bisthiazole solution at 416 nm, indicating that the phenyl and the heterocyclic moieties in PBT are highly conjugated.

Because PBT films, and blends containing PBT are often cast from methanesulfonic acid, they inevitably contain some residual acid. It is therefore important to study the effect of protonation on the emission spectrum of t-bisthiazole (the model compound of PBT) in chloroform containing varied amounts of trifluoroacetic acid (TFA). We have found that as the concentration of TFA increases, a broad structureless band at 460 nm appears and increases in intensity at the expense of the structured band at 416 nm. However, as the concentration of TFA is further increased, the intensity of the band at 416 nm increases while that at 460 nm decreases and nearly disappears when the solvent is 100 percent methanesulfonic acid.

In collaboration with Drs. Ted Heilweil and Rich Cavanagh of the Molecular Spectroscopy Division, we have also measured by picosecond spectroscopy the lifetimes of electronically excited PBT in methanesulfonic acid, and t-bisthiazole in chloroform containing varied amounts of TFA. The lifetime for PBT was found to be 130 ps. The lifetime for t-bisthiazole was 120 ps in pure chloroform, increased to 185 ps in chloroform containing 2% of TFA, but decreased to 142 ps in pure TFA.

Evanescent Wave Induced Fluorescence Spectroscopy of Adsorbed Polymers

The importance of adsorption to problems in areas such as adhesion, flocculation, chromatography, and biological fouling has spurred considerable interest in the adsorption of macromolecules. Theories detailing the adsorption of linear chains onto surfaces using computer simulation methods based on a partition function approach and using analytical methods based on scaling theory are described in the literature. In comparison to theoretical results, experimental results on polymer conformation at the liquid/solid interface are scarce.

We plan to probe the conformation of adsorbed polymers by the technique of evanescent wave induced fluorescence. In this experiment, a polymer solution is in optical contact with a solid substrate. Laser light is coupled into the substrate at an angle appropriate for total internal reflection at the polymer solution/substrate interface. The index of refraction of the substrate must be greater than the index of refraction of the polymer solution for total internal reflection to occur. Concomitant with total internal reflection is the creation of an evanescent wave in the interfacial region. The evanescent wave penetrates the polymer solution with an intensity that decays exponentially with distance normal to the interface. The decay rate depends on the internal reflection angle, the indices of refraction of the solid and solution, and the wavelength of light. When polymers labeled with a fluorescent dye adsorb on the surface of the substrate, chromophores near the surface will be preferentially excited by the evanescent wave. By measuring the fluorescence intensity as a function of penetration depth of the evanescent wave, the concentration gradient of chromophores normal to the surface can be obtained.

We have installed a thin film optical waveguide as our substrate. A waveguide has two advantages over a prism. The fluorescence signal is enhanced due to the numerous internal reflections and the determination of the reflection angle is more precise due to the discrete guided wave modes. Preliminary experiments have confirmed the generation and detection of fluorescence induced by the evanescent wave. Solutions of polystyrene that are fluorescently labeled exclusively at the ends will be studied to determine the extension of polymer tail ends from the surface of the waveguide. The chemistry of labeling a polystyrene chain with a fluorescent group has been established. In addition, the molecular weight characterization of end labeled polystyrene will be accomplished by a gel permeation chromatography apparatus installed specifically for this study.

Fluorescence Studies of Polymer Solutions

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

Dynamics of Polymer Chains

The dynamic behavior of polymer chains is important to improving both characterization and processibility of polymers. The principal methods used to estimate molecular weight, in particular gel permeation chromatography, 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.

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

MECHANICAL PERFORMANCE OF POLYMERS

The approximate 8% annual growth of polymeric materials results from substitution for other materials owing to enhanced properties at reduced costs, the expanded need for all materials due to growth in population and economic activity, as well as new products that rely on unique properties of polymers. Important to wider use and acceptance of plastics is a firmer understanding of performance limitations and processes that affect durability. Full exploitation of plastics has not been realized due to the lack of adequate data and models upon which to design for long-term use and to tailor materials for specific applications.

The objectives of this task are to provide data, test methods, and standards for evaluation of long-term mechanical performance of polymeric materials and determination of those factors that limit performance. The approach is to identify and analyze principal failure mechanisms of commercially important thermoplastics and elastomers under mechanical stress, to determine the effects of chemical structure and fine structure morphology on mechanical properties and failure mechanisms, and to develop constitutive relationships that serve as the basis for accelerated test methodology and lifetime prediction.

The approach to development and verification of predictive models of mechanical performance is: (1) identify the principal molecular mechanisms and processes associated with deformation and failure and establish their relationships with molecular structure and fine texture; (2) evaluate models for degradation of mechanical properties and for extrapolating short-time measurements to predict long-term performance; and (3) model mechanical properties and failure using time dependent constitutive equations.

Joint programs on performance of plastics have been established with other government agencies which are fostering the use of plastics in areas of national concern. A joint program with the Air Force is applying advanced characterization techniques to elucidate the structure of molecular composites formed by combining rigid-rod polymers with thermoplastic matrix materials. This project is concerned with establishing the relationships among the molecular structure, fine texture, mechanical properties, and performance of these materials. Test methods for evaluating the performance of elastomers used in tank track pads are under development in a joint project with the U.S. Army Tank & Automotive Command.

FY 86 Significant Accomplishments

- A nuclear magnetic resonance technique has been developed and applied to determine the partitioning of chain ends and branches between the crystalline and non-crystalline regions of polyethylenes. Side groups (branches) in polymers can greatly affect mechanical properties and performance. A major problem in predicting such effects is that branches may be concentrated in regions of crystalline polymers.

- A joint project with the Gas Research Institute is producing standard polyethylene materials and components of gas distribution plastic piping and joints. The standards are to be used in laboratory studies by the gas utilities industries on mechanical properties and long term performance of polyethylene components. Mechanical properties characterization was conducted on the standard materials to ensure uniformity throughout the large sample of polyethylene piping and joints which are to be made available through the NBS SRM program.

- The physical aging of polymer glasses and their failure behavior under conditions of tensile creep is under investigation. It has been observed that the creep response curves did not agree with recent predictions and a method has been developed to predict long term failure behavior using short time tests.

Characterization of Polymer Structure and Deformation Processes

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Knowledge of the molecular mechanisms and structural changes associated with deformation during and subsequent to processing polymeric materials not only provides the basis for development of test methods for prediction of long-term performance and for quality control, but also provides insights into the selection, processing, and design of materials with improved mechanical properties and performance. A major part of the Group's effort is the development and utilization of advanced techniques to elucidate the structure of polymers from the molecular level to microstructure. Vibrational spectroscopy and solid state nuclear magnetic resonance are used to determine the chemical and physical structures of semicrystalline and amorphous polymers, as well as molecular composites. Calculational approaches are used to predict the spectral signatures of polymers as a function of conformations determined from energy minimization calculations. In particular, the minimum energy conformations of lattice defects thought to be involved in mechanisms associated with mechanical deformation as well as other physical processes are analyzed. Associated with these calculations is an experimental program to produce single extended polymer molecules, or small polymer fibers on substrates which are suitable for investigation by tunneling electron microscopy. The size scale of such specimens are similar to those treated in calculations. Construction of a tunneling electron microscope is well under way. This microscope will be used to investigate the architecture of copolymers and branch distribution in polymers. Better methods are needed to measure branching in polymers as this aspect of molecular structure, such as in linear low density polyethylenes, can lead to enhanced mechanical properties.

Major improvements have been made in the nuclear magnetic resonance instrumentation. The 200MHz spectrometer has been equipped with a new computer system, and deuterium NMR capability has been acquired. The 60MHz instrument has been upgraded with a new computer, and a superconducting magnet is under procurement. The completion of these instrumental modifications will upgrade our NMR capability to state of the art.

A project was initiated in this fiscal year to investigate the structure and mechanical behavior of physical polymer gels. These materials, formed from solution, obtain their properties through physical molecular contacts, rather than chemical linkages, as for example, in polymer networks. The mechanical properties of these gels are sensitive to the state of aggregation and, through modeling, provide a means of assessing various structural models. It has been shown that the mechanical properties are sensitive to the amount of solvent present in the gel, an aspect that heretofore had not been known.

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

Upon being cooled from the molten state, polymers crystallize in the form of spherulitic structures which evolve progressively from lamellar chain-folded single crystal precursors. Fully developed spherulites consist of a radiating array of long, narrow (on the order of 1μm) lamellae. The reasons why the single crystal precursors degenerate into spherulites remain to be fully elucidated. A central feature of the phenomenological theory of polymer spherulite growth advanced in the mid-1960s was the role played by segregated "impurities" (low molecular weight chains, atactic chains). The main postulate of the theory was that the segregation of impurities at the lateral growth faces of the precursor lamellar crystals gives rise to cellulation at these faces and hence to a breakdown of coherent lamellar growth. As indicated in a later review and discussion, the theory did not specifically account for a salient feature of the transitional morphological changes manifested in the evolution of the precursor crystals into spherulites, namely the profuse splaying of lamellae. Furthermore, the role of impurity segregation in the evolution of spherulites has been questioned of late with particular reference to the formation of isotactic polystyrene spherulites. A main difficulty confronted in the study of the fine structural details of the early transient stages of evolution of spherulites in bulk polymer, with the object of determining the nature of the growth processes involved in their evolution, is that these structures are relatively inaccessible to <u>direct</u> electron microscopical examination except in very thin films in which the three-dimensional pattern of development of the spherulites is seriously obstructed. Recent work in this laboratory has led to the observation that it is possible to "excise" isotactic polystyrene (IPS) spherulites at various stages of development from bulk polymer. This capability stems from the fact, discovered in some exploratory experiments, that whereas amorphous IPS dissolves readily in amyl acetate, crystalline IPS does not do so. Because the glass transition temperature of IPS is fairly high (T_g about 90°C), the polymer can be readily quenched to the amorphous state by rapid cooling. Accordingly, the growth of spherulites in bulk polymer samples can be arrested at different shapes of development by rapidly cooling partially crystallized samples to room temperature. Addition of excess amyl acetate to such samples, which contain the spherulitic structures dispersed in a matrix of amorphous polymer, results in the dissolution of the matrix. The crystalline aggregates remain in suspension in the solvent and can thus be conveniently isolated for examination either with a transmission or a scanning electron microscope depending on their thickness. Such a study is currently being pursued.

Partitioning of Chain Ends and Branches Between the Crystalline and Non-crystalline Regions of Melt-Crystallized Polyethylenes

The experiments utilize a) proton-carbon cross-polarization (CP) techniques, b) the differentiation in the carbon spectra of crystalline and non-crystalline carbon resonances, and c) reasonable assumptions about proton-proton spin diffusion in order to establish the morphological position of defects such as chain ends or branches.

Results of the partitioning studies can be summarized as follows: 1) In several samples which were slowly cooled (1° per minute) from the melt, the concentration of chain end methyl and terminal groups in the crystalline regions fell to 76% and 62%, respectively, of the original overall average concentration. This means that these end groups are preferentially, but not severely, excluded from the crystalline regions. Also, these results imply that the ratio of crystalline to non-crystalline concentrations is very much a function of the total crystallinity.

As to the branch concentrations in the <u>crystalline</u> regions, in the systems which have been analyzed fully to date, the methyl branch concentration (4.2 branches per 1000 carbons) is 37% of the average overall branch concentration whereas this percentage is 16% in a sample of hydrogenated polybutadiene (17 branches per 1000 carbons) and less than 10% in an ethylene/butene copolymer (2.6 branches per 1000 carbons). Thus, it is clear that ethyl branches are more excluded from the crystal than methyl branches, which, in turn, are more excluded than methyl and vinyl end groups. A rather surprising result has been obtained recently on an ethylene/hexene linear copolymer having butyl branches. In this material, the crystalline region seems to contain a higher concentration of butyl branches, relative to the overall average, than was found for ethyl branches. We are currently pursuing certain questions about the test methodology used for butyl branches. The polyethylenes with branches having four or more carbons present a problem in the analysis since resonances of the methyl carbons from chain ends and branches are superimposed. These resonances are distinct for methyl and ethyl branched polyethylene.

We have also looked at samples which were exposed to ionizing radiation. One set of samples was sealed in vacuum and placed in a gamma-ray source. Two other samples of ultrahigh molecular weight LPE were subjected to rather intense electron beam irradiation under nitrogen. No differences in reaction chemistry were observed with the two kinds of irradiation. The production of methyls and interior vinylenes along with the early disappearance of any terminal vinyls was observed. Also a loss of crystalline perfection was indicated. Some crystallinity could be restored by annealing; however, the partitioning of defects such as the interior vinylenes was unaffected by annealing as one would expect if chains were highly cross-linked, i.e. if a carbon in a crystalline environment was forced to remain in a crystalline environment.

^{13}C Spin Diffusion at Natural Abundance

The object of this work is to examine ^{13}C-^{13}C spin exchange in crystalline materials having natural abundance populations of ^{13}C nuclei. A strong motivation for this work was the recognition that due to the dilute nature of the ^{13}C spins (1.1% at natural abundance), spin exchange interactions should be weak and governed by statistical distributions. Therefore, ^{13}C spin exchange should be a reasonable probe over distances of 0.5-1nm during times of 1-100s. This technique was successfully applied to cellulose in which polymorphy was demonstrated by the lack of spin exchange between certain resonances.

In linear polyethylene, a temperature-dependent spin-exchange rate was observed. The only explanation for this is that internuclear distances between ^{13}C nuclei are time dependent, i.e. the chains are being transported through the crystal lattice, even at room temperature. Through modeling, a crude estimate of transport rates was obtained. The chain transport inferred from the data was not consistent with uniform transport described by unbounded diffusive motion. Failure of this model might be attributed either to a wide distribution of crystalline stem lengths or to the bounded nature of chain transport in the crystalline lattice.

Polystyrene Gels

Isotactic polystyrene (i-PS) gels exhibit unusual mechanical behavior and observations in other laboratories claimed evidence for a new crystalline phase in the gels, periodicities of the order of 300nm, and PS/solvent complexes.

We investigated these gels at ambient temperatures using both ^{13}C and proton NMR to test the various structural models. From the proton NMR and from the stoichiometry of the original solutions, we concluded that 46% and 52% of the i-PS appeared rigid on a time-scale of 10 microseconds in gels made up of 25% by weight PS in cis- and trans-decalin, respectively. In gels made from 10% by weight PS, the fraction of PS which appeared rigid increased to 51% and 64% in cis- and trans-decalin, respectively. The increase in the rigid fraction with decreasing initial concentration of PS is evidence that points of condensation are more widely separated at lower concentrations and that a larger fraction of the total chain length is identified with each condensation site.

The ^{13}C NMR experiments performed on the gels are more qualitative because cross polarization techniques were employed in the absence of a detailed knowledge of the proton relaxation dynamics. Cross-polarization techniques were required in order to obtain sufficient sensitivity. The carbon spectra of non-spinning gel samples indicated that the proton-decoupled linewidth of the i-PS carbons was very similar to that of the i-PS glassy solid, which, in turn, is close to the linewidth of the crystalline solid. Thus, the more rigid PS chain segments in the gels exhibit mobility similar to the normal condensed phases of PS. The other important finding from the CP experiments was that the broader resonances did not include any unusually larger contribution in the aliphatic region where decaline (in any possible PS/solvent complex structure) would appear. It is, therefore, not likely that there is any PS/solvent complex in the more rigid PS regions. For this conclusion we also cite the motional rigidity indicated by the PS linewidth. If a complex existed, then the packing would probably contain more free volume so that more PS chain mobility would be expected.

These findings significantly restrict the models available for describing the gel phase. A fringed micelle model seems reasonably consistent with the NMR data but inconsistent with periodicities of the order of 300nm in the following naive sense: Suppose the sites of PS condensation were distributed on a cubic lattice having periodicity x. Then the characteristic domain dimension of this condensed phase would be close to x/2 in the 25% gels (approximately 1/8 of the total volume is solid PS). If the periodicity is 300nm, then the condensed phase would be 150nm across. Such a large dimension should yield a condensed PS phase identical to the normal condensed phases. Moreover, if this phase were crystalline, WAXS should reveal this...but WAXS reveals no crystalline peaks. Furthermore, proton dipolar relaxation times in the gels are significantly shorter than in the glass or crystal. Therefore, a small (less than 10nm) domain size is suggested.

Estabishing Connections Between Butyl Side Branches and Resistance to Slow Crack Growth in Linear Low Density Polyethylene

The behavior of side branches is important in understanding the useful properties of linear low density polyethylene, particularly one with a concentration of a few branches per 100 main chain carbon atoms that has been found to have superior crack resistance in critical applications such as pipe for the distribution of natural gas. Such pipes are expected to last for many decades and it is essential to understand their behavior in order to control the processing that leads to stable, safe, and uniform quality pipe for this large scale operation. The work is being done in consultation with the Gas Research Institute.

A working hypothesis suggests that the interactions between the butyl group and the polyethylene crystal alter or prevent the chain transport mechanisms which lead to crack formation. This hypothesis is very difficult to investigate experimentally because the important type of cracks may form slowly over a period of years.

The processes by which the butyl branches lead to crack resistance can be modeled with the help of crystallographic defects and the observable morphological features of the polyethylene in the pipe.

Side branches, from methyl groups to butyl groups and even longer, can be accommodated in the crystal and even diffuse through it. We have calculated the energy required to place a butyl side branch in the crystal. Barriers to movement along paths involving defect motion appear to be low enough that the defect can move by utilizing energy available from macroscopic strain fields or from forces transmitted along the chain. It is reasonable to expect that such forces can move the side branch without necessarily causing the chain to break. This possibility is being investigated by computer modeling of the conformations of the chains in a crystal in the immediate vicinity of an incorporated side chain.

Ethyl branches can be accommodated by smooth bending of the surrounding chains, without the introduction of gauche dihedral angles. Butyl and longer branches require that the adjacent chains bend around the branch and this requires a row of jog like conformations with gauche bonds in some of the chains.

This row of jog-like conformations has been recognized as an ordinary screw dislocation loop with properties that have been investigated in metal crystals, except that in polymers the dislocation line encircles only one plane of molecules. The introduction of a few other defects for which specific energies and motional properties are or can be defined allows the problem to be treated in terms of the defects rather than requiring the calculation of the detailed conformations of many chains. This produces a tremendous simplification of the problem and opens the possibility of developing realistic and tractable models for the molecular scale processes in the vicinity of a growing crack tip.

Origin of the Longitudinal Acoustic Mode in Polyethylene

In crystalline polyethylene in the forms often used, a single molecule passes from crystalline regions with long all-trans segments through regions with folds or other conformations. The longitudinal acoustic mode vibrations provide information about this structure. The effects of the non-trans regions on the frequency of the observed longitudinal acoustic mode were investigated by calculating the behavior of a polyethylene chain in a lattice with periodically spaced crystallographic defects or folds.

The defects considered are the dispiration loop, the disclination loop, the dislocation loop (all loops encircle only one chain), folds with nearest reentry to the crystal in multiple fold systems and chain twist boundaries.The atomistic models examined are much more extensive than those considered previously and, as a result, required large computational power. The force field and the lattice geometry, together with minimum energy calculations, determine other physical parameters relevant to the model, such as moduli of crystalline and defect segments, longitudinal stresses at the boundaries, and force and mass perturbations.

The longitudinal acoustic mode frequencies were found to be inversely proportional to the sum of the length of the all-trans segment and to a quantity 2Δ which represents the masslike effect of the defect region on the LAM vibration. Delta was found to have a value of 3.75 ± .25 angstroms. The internal structural details of the defects and the conformations of adjacent chains are relatively unimportant, as long as minimum energy conformations of the defect region are used.

Vibrational Spectra of Defects in Crystalline Polyethylene

Polyethylene in useful forms like molded objects, films or ultra high strength fibers is known to contain a significant fraction of the polymer in conformations which do not have the all-trans arrangement of the perfect crystal. Vibrational spectroscopy promises to provide information for the characterization of these conformations.

To investigate this possibility, the spectrum of polyetheylene crystals containing crystallographic defects in their minimum energy conformations was calculated and compared with experimentally observed spectra. This was done for folds, dispirations, disclinations, dislocations, and twist boundaries.

Each defect produces many new bands in the vibrational spectrum of polyethylene. In many frequency regions, two or more defects contribute to the intensity of observed bands. There are a few bands which are characteristic of one defect or another, but such bands are generally weak and close in frequency to other bands. In ordinary experimental spectra, the result is that most of the vibrations associated with the defects contribute to a broad background. An important exception is the defect associated bands which fall at a frequency that lies in a gap between dispersion curves of the crystal. Twist boundaries have such a vibration. It is observed experimentally, particularly in rapidly cooled samples.

Correlation spectroscopy provides the possibility of separating and observing some of the defect associated modes. Other relevant information may be gleaned from the spectra of crystalline cyclic alkanes where known non-trans conformations exist, or from molecules which contain alkane sequences as branches, as do some biological molecules, or as blocks in a linear copolymer. An interesting example of this class is a triblock of an alkane sandwiched between two fluoro-alkane segments investigated by workers at IBM, San Jose. We predicted a band associated with the twist of the alkane segment which was subsequently found in the infrared spectrum.

We are now cooperating with workers at Oak Ridge National laboratory in the development of molecular dynamics calculational techniques for determining the spectra of defect conformations of polyethylene chains. This offers the possibility of studying the widths of the bands associated with particular frequencies and of characterizing the interactions between vibrations with nearby frequencies but different normal coordinates and other non-linear processes in a more informative way than conventional vibrational analysis permits.

Small Polymer Fibers, Thin Polymer Films, and Single Polymer Molecules

The scanning tunneling microscope offers the possibility of producing images of polymer molecules on a conducting substrate. A microscope for this purpose is now being constructed with the help of workers in the Physics Department of the University of California at Santa Barbara.

A repertoire of techniques for producing very small fibers, thin layers of polymers and isolated polymer molecules has been developed. Thin films or networks of polymer molecules suitable for examination in a transmission electron microscope have been prepared on carbon films thinned by exposure to a glow discharge in oxygen until they contain small holes or cracks across which the polymer is stretched. Ruthenium tetra-oxide techniques for staining the polymer molecules have been developed. High resolution, high magnification transmission electron microscope techniques that produce resolutions under 10 angstroms have shown that films and networks produced by different polymers (polyethylene, polyetheretherketone, polystyrene, polyisobutylene, poly gamma benzyl glutamate) have different characteristic features, although fundamental limits of the performance of the transmission electron microscope do not allow individual polymer chains to be imaged in detail.

A program written at Arizona State University for calculating the image of a known molecular structure was installed in the Cyber 855 and is being used to investigate the images expected for the known transfer function parameters of the electron microscope. The program calculates a 128 by 128 pixel image of a sample containing several layers of atoms by a method that is equivalent to solving the time independent Schrodinger equation by the Cowley-Moodie method and calculating the effects of parameters including spherical and chromatic aberration, defocus, electron wavelength, radius of the objective aperture, specimen thickness, beam divergence and sample orientation. The program provides increased capability to interpret polymer structure from micrographs, where the images are complicated by changes in the sample produced by the electron beam, the presence of heavy atoms used to decorate the chains, and the presence of a substrate to support the chains.

A very efficient method for producing through focus pictures needed to interpret the electron microscope images was developed. It involves tilting the sample so that different parts of the field of view have different amounts of defocus. Since the most useful contrast is obtained at a particular but difficult to achieve level of defocus this technique has proven to be efficient and useful for these samples.

Precipitation of polyethylene samples spanning molecular weights from around 52,000 to over 5 million showed that the molecules interacted and formed network like features at concentrations as low as 10^{-3} gm/ml for the 5 million molecular weight polyethylene, while the critical concentration predicted theoretically at which the random coils in solution would be expected to overlap is about 10 times higher at each molecular weight. This is consistent with reports in the literature that measurements of elongational flow show evidence of molecular interactions well below the critical concentration.

Mechanical Properties Measurement and Modeling

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The mechanical performance and behavior of polymeric systems covers a modulus, G, range including the gel-like state (G~10KPa), rubbery state (G~1MPa), semicrystalline polymers (G~.3GPa) and the glassy state (G~1GPa). Members of the Polymer Division staff are conducting research to characterize relationships between the molecular and continuum physics of appropriate polymer systems as used to model mechanical properties.

On the basis of investigations of the mechanical behavior of polymeric systems which exhibit a variation of over 5 orders of magnitude in modulus, major contributions are being made to the understanding of the molecular and continuum physics required to predict and/or describe the mechanical performance of macromolecular materials.

A Reduced Variable Approach to Relating Creep and Creep Rupture in PMMA

The description of the viscoelastic and creep rupture behavior of polymers subjected to large stresses has received considerable attention. Kinetic and reaction rate models, which have successfully described the failure behavior of polymers subjected to monotonically increasing loading histories, appear to be unsuitable when the loading history is more complicated. Similarly, there have been several successful attempts to correlate the nonlinear viscoelastic response of polymer glasses under monotonic loading histories using the concept that the applied stress, or strain, simply shifts the viscoelastic spectrum along the time axis. That is, the creep, or stress relaxation, curves at different stress (strain) levels can be superposed to form a master curve by a shift, a_σ, along the log time axis.

In addition to the consideration of the time dependent behavior of polymers, it is know that the mechanical response of polymeric glasses is also dependent upon the thermal history to which they have been subjected. It has been shown that, to a first approximation, the effect of a change in the volume of the glass is to shift the viscoelastic spectrum along the time axis. This phenomenon is generally referred to as physical aging.

While much work has been done to describe either the failure behavior of polymers or the effects of stress, strain, or volume on their viscoelastic response, little work has been directed toward studying both aspects simultaneously. We have begun a program designed to address both the issue of physical aging in polymeric glasses and their failure behavior under conditions of tensile creep. In the initial stage of this work the creep behavior at relatively large stresses has been examined for specimens of polymethyl methacrylate (PMMA) which were subjected to two widely different thermal histories. Specimens were prepared from one sheet of commercial grade PMMA which is known to have been manufactured more than five years prior to its use. Tensile specimens prepared from the sheet were divided into two sets. One set was used as-received (aged at room temperature for five years). The second set was heated above the glass transition temperature to 120°C and held at that temperature for one hour, and then removed from the oven and allowed to cool rapidly in air to room temperature. This heat treated (rapidly cooled) set was stored at room temperatures for at least one week prior to mechanical testing. Creep tests were then done for a range of applied engineering stresses of from 30 to 60 MPa. All experiments were done at 22.5 ± 1°C in a room where the relative humidity was maintained between 40 and 50 percent. Except at the very smallest loads, the creep experiments were continued until fracture occurred.

It was found that when represented in terms of the creep strain the data obtained at different stresses could be superposed onto mastercurves by a shift along the time axis with no vertical shift required. The shift factors along the time axis were found to be the same for both sets of creep curves, the only difference being that the entire mastercurve for the rapidly cooled specimens was shifted to shorter times by a factor of 2.5 relative to the mastercurve for the well aged specimens. On log - log coordinates a plot of the horizontal shift factors versus applied stress yielded a straight line over the entire range for which data were obtained. A log - log plot of time to failure versus applied stress also resulted in a straight line over the range of data for which the specimens actually failed. In the absence of unknown environmental effects such plots should be useful to predicting a lower bound to the long time failure behavior of PMMA under tensile creep rupture conditions.

When represented in terms of the creep compliance, superposition of the two sets of curves is still possible, but now requires a vertical shift, the shift factors along the time axis being the same as before. The vertical shift required was found to be simply the ratio of the stress corresponding to the curve being shifted to that of the reference curve ($b_s = \sigma_a/\sigma_r$).

The master curves were also examined to determine whether the creep response could be fitted with a fractional exponential function where the exponent is equal to about one third. It was found that the data could not be fit using a single fractional exponential, irrespective of the exponent. Rather it was found that all the data could be fitted within an error of 5-7 percent using the sum of two fractional exponentials. In this case the only difference required in the fitting parameters between the two mastercurves was a factor of 2.5 in the horizontal shift factors.

Additionally, in theories of crack growth a relationship is used which states that the time to failure for creep at constant stress multiplied by the strain rate at failure should be a constant. An important observation here in that regard is that the strain at failure was found to be essentially constant (10-12% strain) for nearly all the specimens tested. This fact taken with the observations that the shape of all the creep curves were the same and the vertical shifts required to superpose the compliance data were equal to the ratio of the applied stress to the reference stress implies that such a relationship is true for the two preparations of PMMA under investigation here.

Finally it is suggested that in systems for which it is true that the product of the time to failure and the strain rate at failure is a constant, the reduced variable approach described in this paper can be used to predict the long time failure behavior of polymeric glasses using short time tests.

Constitutive Equation for Non-linear Viscoelastic Behavior of Incompressible Materials

In an attempt to overcome some of the inadequacies of the BKZ theory on the description of the non-linear behavior of isotopic materials, we derived a new constitutive equation. For the case of simple shearing flow the shear stress $\sigma_{12}(t)$ is given by the following expression

$$\sigma_{12}(t) = -\int_{-\infty}^{t} H_{*}(\lambda(t)-\lambda(\tau),\ t-\tau)\,d\tau + \int_{-\infty}^{t} F_{*}(\lambda(t)-\lambda(\tau),t-\tau) \int_{\tau}^{t} (\lambda(\zeta),\zeta)\,d\zeta\,dt$$

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

There is a characteristic time t_1, which depends on the material. If a material has been in a strained condition for time greater than t_1, then it can be considered as being at rest for all time.

This equation has been successfully applied to already published data.

Characterization of the Nonlinear Viscoelastic Behavior of Epoxy and Rubber Toughened Epoxy Resins

Cast cylinders of an epoxy and its CTBN rubber toughened analogue have been tested in single step stress relaxation in torsion at constant length. Both torque and normal force responses were measured at times from 0.1 to 3,355s and at strains of $\lambda=0.0025$ to $\lambda=0.08$. While both materials exhibit nonlinear behavior in the torque response at ≈2-3% strain the modulus G(t) of the untoughened resin decreases more rapidly than does that of the CTBN modified material. Data were obtained on various two step stress relaxation experiments and the behavior were analyzed with the new constitutive equation.

Non-linear Shear Behavior of a Polyisobutylene Solution

Single and multistep stress relaxation experiments were obtained on a 15% polyisobutylene solution (B-200) in Opanol. Some of the wiring and pickup transducers were changed on the Rheometrics Mechanical Spectrometer, so that input signals and the responses could be accomplished with the aid of a computer. This minimized errors on the introduction of the steps due to overshooting, and cut the time of the introduction of the step by a factor of 20. The data were analyzed with our new constitutive equation. The three functions were evaluated for times ranging from .2 to 1000 sec and shear strains from .5 to 20. All the terms for strains greater than 1 were highly non-linear. The characteristic time for this solution at 25°C is about 5,000 seconds, while the stress in a stress relaxation experiment at 1000 sec after the introduction of the step was about 500 smaller than its value at t=.2 sec. As yet, we do not have a molecular explanation for this persistent memory on the previous strain history.

The Effect of X-Rays on the Polycarbonate Substrate of X-Ray Calibration Standards

In a new type of X-ray calibration standard issued by the National Bureau of Standards (NBS), thin uniform layers of silica-based glasses containing certified amounts of specific elements are deposited by ion beam coating on a polycarbonate (PC) film substrate. The PC substrate was selected primarily because it was essentially free of trace elements. This substrate is stable when exposed to relatively low intensity X-rays from secondary target emitters in energy dispersive (EDX) spectrometers. However, PC films irradiated with primary X-rays in a wavelength dispersive (WDX) spectrometer show radiation damage, such as color changes in the film (from milky white to brown), embrittlement, and, in some cases, splitting along the parallel striations visible on one side of the film.

As radiation damage will affect the service life of calibration standards, it was necessary to determine the effect of X-rays on the physical strength of the PC film substrate (no problems with the glass coatings on the substrate were observed). Specimens for tensile measurements were cut from the polycarbonate film used as the calibration standard substrate.

In the manufacturing process, the membranes are prepared by a solvent casting technique and are stretched by a factor of 3:1 in the machine direction. The film is therefore partially crystalline and has anisotropic mechanical properties in the machine versus the cross-machine direction. Striations, parallel to the machine direction, are visible on one side of the film. Tensile test specimens were cut both parallel and perpendicular to the machine direction based upon the orientation of the striations. The specimens were cut from the filter membranes before irradiation; after irradiation films were often too fragile to cut.

Specimens were irradiated in both WDX and EDX spectrometers. In the WDX spectrometer the specimens were exposed to unfiltered direct radiation from a chromium-target X-ray tube operated at tube powers (kV x mA) from 3-0.2 kW. In the EDX spectrometer the specimens were exposed to secondary target emitters (either molybdenum or germanium) excited by a tungsten-target X-ray tube operated at 40kV and 30 mA.

Two tensile properties were measured: (1) the strain at break, and (2) the stress at break. The value of each property depended upon whether the specimen was cut parallel or perpendicular to the machine direction. With the exception of the stress at break for specimens cut perpendicular, the effect of X-rays on the measured property was cumulative: specimens irradiated with the same X-ray tube energy (kW-min), no matter what the irradiation time, the tube power, or the tube voltage, showed approximately the same tensile change. For specimens cut parallel to the machine direction, both the stress at break and strain at break showed a steady decrease with irradiation until, at an energy of 100 kW-min, the value of either property was approximately one-half that of the unirradiated material.

Specimens cut perpendicular to the machine direction exhibited a different behavior. Irradiation had no effect on the measurement of stress at break: all specimens, unirradiated or irradiated, had the same stress at break, 35 MPa (standard deviation, 2 MPa). At an energy of 100 kW-min the strain at break was approximately one-fourth that of the unirradiated polycarbonate.

The tensile measurements show that primary X-rays will degrade the PC film. The greater change in strain at break with irradiation for specimens cut perpendicular to the machine direction suggest that the deterioration in mechanical properties will be greater in this direction. In using calibration standards with a PC substrate it is suggested that a standard be handled with extreme care once irradiation has begun, and that a record be kept of cumulative X-ray tube energy to which the standard has been exposed.

Mechanical Durability of Polymeric Materials

D. L. VanderHart, G. W. Bullman, J. M. Crissman, K. M. Flynn, G. B. McKenna

The objectives of this Subtask are to develop measurement methods and models of long term mechanical performance and to conduct joint projects with other government agencies on mechanical durability issues of concern to those agencies. Joint activities with other agencies provide opportunities to evaluate various approaches to mechanical durability on materials with known performance histories.

The durability of rubber tank track pads has been of concern to the Army, and a joint project has been established to develop predictive methods for performance. The failure behavior of filled rubbers under static and dynamic loads is being investigated.

Reference Standard Polyethylene Resins and Piping Materials

The Gas Research Institute is sponsoring a program at NBS to provide reference materials for use in research pertaining to natural gas distribution systems. In addition to the pigmented and unpigmented polyethylene resins, described elsewhere in this report, this program includes the procurement and characterization of piping and joints prepared from the pigmented resin. Piping in three sizes (1.27, 5.08, and 10.16 cm diameter) and two types of tee joints have been received and characterization of these materials is underway. Tensile tests and/or density measurements have been done on each size of piping and each type of joint.

From the 1.27 and 5.08 cm diameter pipe ten specimens were prepared by cutting rings from five different locations along one 25cm long section. Each ring was then cut in half. From the 10.16 cm diameter pipe, five specimens were cut from one ring section. Density measurements were then made with the displacement method using degassed distilled water at 22°C. The average density for all 25 specimens was found to be 0.938 g cm^{-3} with a standard deviation of 0.001 g cm^{-3}. The experimental error using this method is estimated to be no greater than ± 0.001 g cm^{-3}. These measurements indicate that there is no significant difference in density among the three sizes of pipe.

One butt tee joint and one socket tee joint were also examined for uniformity in density. Six specimens were taken at different locations from one butt tee joint and six from one socket tee joint. For the six pieces from the butt tee joint, the density ranged from 0.928 to 0.939 g/cm^3, whereas, for the socket tee joint, the range was from 0.921 to 0.940 g/cm^3. In both cases the lowest densities recorded were for the pieces taken nearest the point on injection and the highest values were obtained for the pieces taken from a point on the inside wall well away from the point of injection. Two tensile properties, the yield stress and strain at yield, were examined for two of the three different sizes of pipe. The largest diameter pipe was not included due to a lack of load capacity in our test machine. Six pieces of the 1.27 cm (0.5 in) diameter pipe and four pieces of the 5.08 cm diameter pipe were selected at random from the two lots of pipe. In order to obtain a measure of the specimen to specimen variability within the two lots of pipe, 10 specimens of the 1.27 cm diameter pipe and 6 specimens of the 5.08 cm diameter pipe were tested at one strain rate (81% per min). The average yield stress for the ten specimens of 1.27 cm diameter pipe was 16.4 MPa with a Standard Deviation of 0.15 MPa. The strain at yield was found to be essentially the same for all ten specimens (ε=0.125). For the larger diameter pipe, the average yield stress was 17.4 MPa with a standard deviation of 0.2 MPa, while the strain at yield was the same for the six samples tested (0.127) and only slightly higher than for the smaller diameter pipe.

PROCESSING AND RELIABILITY OF POLYMER COMPOSITES

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

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

The overall objective in this Task is to establish the scientific basis for the relationships between the generic parameters associated formulation and processing and the properties important in the performance of the final material. The programs in this Task are divided into three highly interrelated areas: processing, structure, and performance. Projects in the first subtask deal with the development of new process monitoring techniques and the application of these techniques to the study of model systems. This provides both new measurement methods for process monitoring and a better understanding of the events that occur during processing. The second subtask area seeks to bridge the gap between processing and performance by developing techniques to determine the structure of the fabricated material. Both macro-structure (i.e. flaws, defects, phase separated domains, etc.) and micro-structure (the molecular network) are of interest, but most of the work during the past year has focused on the use of neutron-scattering techniques to study the molecular network in epoxies. These techniques are now being applied to the analysis of materials whose processing and performance properties are also being examined. The third subtask focuses on the determination of performance properties for polymers and their composites. The major efforts in this area during the past year have been studies of fiber-matrix bonding and failure behavior of high fracture energy polymers and their composites.

To assist in conducting this broadly based effort, the Task utilizing a number of cooperative programs as well as the assistance of experts who, in some cases, have spent time working in the Division during the last year. A major new aspect of this cooperation was the initiation of an Institute wide Colloquium Series on Composite Materials which brought many world renown scientists to NBS for discussions. The cooperative efforts involve programs with NASA Langley Research Center, the Department of Treasury, and the industrial research laboratories at Hercules, Hexcel, and Texaco. In addition, joint programs were conducted with Drs. A. J. Kinloch at Imperial College (London) and R. S. Stein at the Univ. of Massachusetts. Guest workers and visiting scientists during the last year have included Mr. A. Gilat from the

Ministry of Defense in Israel and Ms. Weijie Su from the Shanghai Institute of Pharma and Tech. in China.

FY 86 Significant Accomplishments

- The capability to measure the complex events which occur during processing has been developed using a variety of techniques. Several model systems have been successfully examined with multiple techniques including one example where six different measurement methods were utilized. This is far beyond the capabilities previously available either at NBS or elsewhere and demonstrates a unique facility that will be exploited in future studies.

- Viscosity changes during cure have been correlated in model materials with the results from four measurement techniques that have on-line potential: ultrasonics, fluorescence, photo-bleaching, and dielectrics. Both similarities and differences have been highlighted as a critical first step toward evaluating the potential of these measurement methods. Proper control of viscosity is the single most important factor in efficient composite processing.

- The molecular mechanism for large strain deformations in epoxies has been shown by neutron scattering experiments to be at variance with current knowledge concerning the deformation mechanisms in rubbers, and other cross-linked polymers. In epoxies cured with short chain amines the average distance between crosslinks in the molecular network stays unchanged even when the macroscopic strain reaches values up to 30%. This result suggests that the deformation mechanism is either defect controlled or unfolding of the network.

- It has been shown that the fracture energy of rubber-modified epoxies is loading rate and temperature dependent, but simple viscoelastic modeling can be used to obtain empirical parameters that depend only on the material. It has been suggested that the volume fraction of phase separated rubber is the critical factor in determining the fracture energy. The empirical parameters of our viscoelastic model can not be correlated with volume fraction alone, and thus new failure models are needed.

Cure Monitoring and Process Control for Thermosetting Polymers and Their Composites

S. S. Chang, B. Dickens, B. M. Fanconi, K. M. Flynn, D. L. Hunston, F. I. Mopsik, J. C. Phillips, F. Wang, and A. C. Lin

The precise monitoring and control of the cure process is an important factor for manufacturing reproducible products that possesses properties suitable for each practical application. The properties of the resin are strongly influenced by the degree of cure and to a lesser extent by the rate and the path of the curing process. It is important therefore to develop cure monitoring techniques both for the laboratory, so cure cycles can be developed, and for on-line applications, so the processing can be monitored and controlled. This is particularly important in the manufacturing of large laminated items where the development of on-line or in-situ cure monitoring techniques will not only provide precise control of the curing process but also increase efficiency and reduce waste by minimizing post-process inspection and reducing rejection rates.

The goal of the NBS program is to support the scientific and industrial communities by: (1) developing improved cure monitoring techniques, (2) maintaining a wide variety of such techniques for the evaluation and calibration of new methods, and (3) studying simple systems with multiple techniques to increase our basic scientific understanding of processing events and to develop models for process control.

During previous years, this program has developed or improved a wide variety of cure monitoring techniques which can be classified in terms of the properties measured:

- Mechanical and Transport Properties
    - Viscosity
    - Dynamic mechanical properties -- torsional braid analysis
    - Ultrasonics
- Thermal Properties
    - Calorimetry -- Differential Scanning Calorimetry
- Electrical Properties
    - Conductance/Resistance
    - Dielectric Properties
- Optical Properties
    - Spectroscopy -- Fourier-Transformed Infrared Spectroscopy,
      -- Fluorescence Spectroscopy
- Other Chemical and Structural Properties
    - Neutron Scattering -- network structure in deuterated materials
    - Chromatography --Size Exclusion Chromatography for molecular volume

In the past year, a new technique, photo-bleaching, was developed (see below), and a number of improvements have been made in the instrumentation or experimental procedure for other monitoring methods. These advances are summarized below together with some of the more interesting results obtained through the application of these techniques.

VISCOSITY. For the viscosity measurements, a new computer program has been developed to more fully automate the instrument. Shear rates are now automatically adjusted to fully utilize the digitization range of the viscosity measurement.

ULTRASONICS. In the ultrasonic measurement, we have successfully developed a technique to apply a thin layer of silicone release agent to facilitate the removal of the cured resin from the quartz substrate rod without causing damage. Experiments show this does not effect the cure results.

DSC. In differential scanning calorimetry, the heat of the cure reaction can be measured in either isothermal or scanning modes. For thermally stable materials, however, the cure may continue for long periods of time even at the highest measurement temperature (200-250 C). Thus an integration of the area of the exothermic peak for a scanning curve may not be sufficient to indicate the total heat of reaction. As an alternative the heat can be more reproducibly defined by closing the thermodynamic cycle, i.e., by ending the measurement on the products at the same temperature as the measurement started on the reactants. The degree of cure for any time or path can then be estimated by normalizing the heat released to the maximum exotherm, since the amount of heat released during the cure is directly proportional to the number of bonds formed.

DIELECTRICS. The use of the time-domain dielectric spectrometer and conductance measurements at 50Hz to monitor cure were described in the previous report. During the past year several experiments have been performed to compare the conductance results with viscosity measurement made during cure on the same material. For the most part the conductance was a strong inverse function of viscosity, but features were also observed that were unique to the dielectric measurements. For example, the amine cured system shown in Figure 1 exhibited in the conductance curve (1D) a dipolar relaxation after gelation. This obviously could not be seen in the viscosity data (1A). In another system (epoxy cured with ethylmethylimidazole), the conductance was found to increase during the early phases of cure where the viscosity was also increasing. This clearly indicates the presence of an ion-forming reaction in the cure chemistry. Clearly a simple interpretation of conductance as a measure of viscosity can be misleading.

FLUORESCENCE. In fluorescence spectroscopy we have demonstrated the use of viscosity sensitive fluorescent molecules as probes for the local microviscosity and the use of a photobleaching technique to determine the diffusion coefficients for a fluorescent dye. In the first technique the fluorescent intensity of an excimer-forming dye decreases with increased viscosity due to a reduction in the excimer formation. Alternatively, the fluorescent intensity of another type of dye is enhanced with increased viscosity due to a reduction in the excited state electronic energy lost through non-radiative processes. An example of the latter case is shown in Figure 1C where the fluorescence is ratioed to that for a viscosity insensitive dye. In the photobleaching experiment, the dye is rendered inactive in a small region by high intensity radiation at an appropriate frequency. The fluorescence in this region is then monitored as it returns to normal by diffusion of the unbleached dye into the sampling volume. The time constant for this change is related to the diffusion constant. By repeating this process, changes during cure can be monitored. An example of this is shown in Figure 1B. For all of these methods an effort is underway to use a light-pipe or a wave-guide to excite and monitor the fluorescence in the interior of the material thus giving an in-situ monitoring device.

Comparisons of Results from Different Methods

The most important and exciting aspect of the work during the past year has been the application of many measurement techniques to characterize the same model systems. By comparing the results, the sensitivity and the applicability of individual methods may be assessed. In Figure 1, the results for curing a diglycidyl ether of Bisphenyl-A (DGEBA) type epoxy, DER 332, with bis-(paminocyclohexyl) methane, BPACM, at 45 C are given for measurements of viscosity, fluorescence intensity, fluorescence recovery after photobleaching, reaction exotherm (DSC), ultrasonic attenuation and conductance at 50Hz.

As shown in Figures 1A and 1C, the fluorescence, the viscosity, and the diffusion coefficient from the photobleaching measurements are highly sensitive to the initial stage of cure. The fluorescence intensity measurement is made with the probe molecule, 1-(4-dimethylaminophenyl)-6-phenyl-1,3,5-hextriene, normalized to the intensity of a viscosity insensitive molecule, 9,10, diphenylanthracene (Figure 1A). The diffusion coefficient is measured with the probe molecule, 1,1'-dihexyl-3,3,3',3'-tetramethylindocarbocyanine perchlorate using the photobleaching experiments (Figure 1C). Interestingly, the increase in the diffusion constant is similar in magnitude to the change in viscosity. The diffusion constant curve is not smooth and its structure may provide useful information.

The isothermal release of the heat for the curing reaction is shown in Figure 1B. As the sample was prepared by melting the BPACM and then mixing it into DGEBA, the curing reaction has already progressed to some extent during the mixing process. Consequently, the DSC thermogram picks up the reaction at a particular degree of cure. The maximum cure at 45 C is about 75% of a fully cured sample at high temperatures, estimated from separate DSC measurements or from heat released in a post-cure process. Both fluorescence measurements also indicate that the reaction starts off at a reasonable rate. The viscosity curve shows a similar pattern although there is a 10 minutes delay to reach 45 C. The conductance curve, Figure 1D, can not be evaluated in this way because temperature equilibrium requires 20 minutes or more (equipment modification has now eliminated this problem). The ultrasonics curve, Figure 1C, on the other hand, has a different shape, but clearly it does not indicate an induction period as might be suspected. Additional studies are now underway to examine this comparison more fully.

Both DSC and dielectric measurements can be used to determine the age or the effect of storage for the sample, i.e. the degree of pre-reaction before the cure process. For example, the conductance curves for three samples, DGEBA catalyzed by 2-ethyl-4-methylimidazole, aged at 23 C are shown in Figure 2, where each curve is shifted in time to match the later part of the cure process (the conductance of each sample is also shifted by an arbitrary amount to separate the curves for clarity). The time shift can be used to construct a cure curve for 23 C. Both DSC and dielectric measurements yield identical curing time constants for the cure reaction at room temperature for both this system and the amine system discussed above.

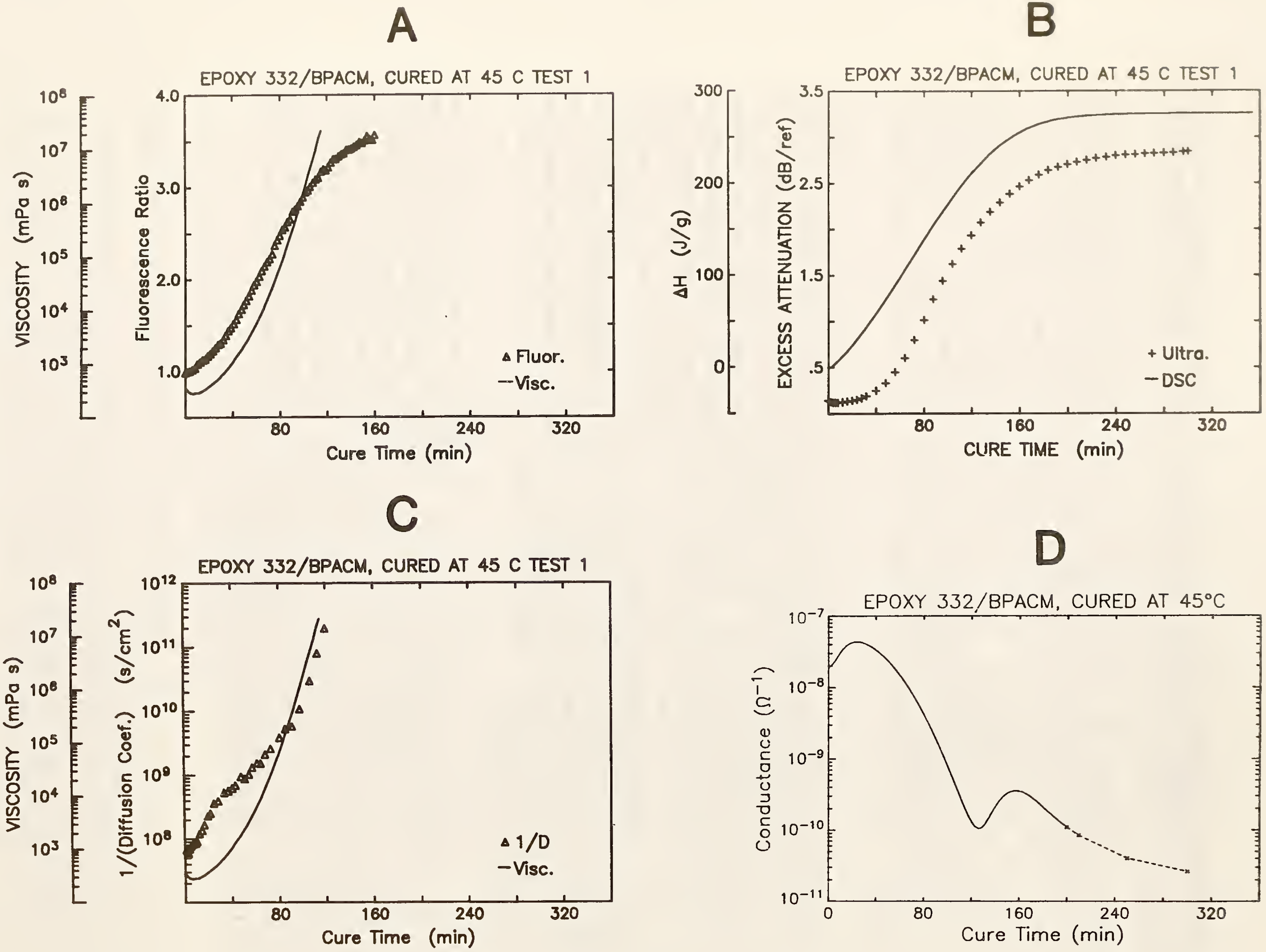

Figure 1: Cure data for epoxy-amine system monitored by six techniques: Viscosity, Fluorescence Ratio, Diffusion Coefficient via photobleaching experiment, ultrasonic attenuation change in shear wave reflection technique, heat generation via DSC, and conductance at 50 Hz.

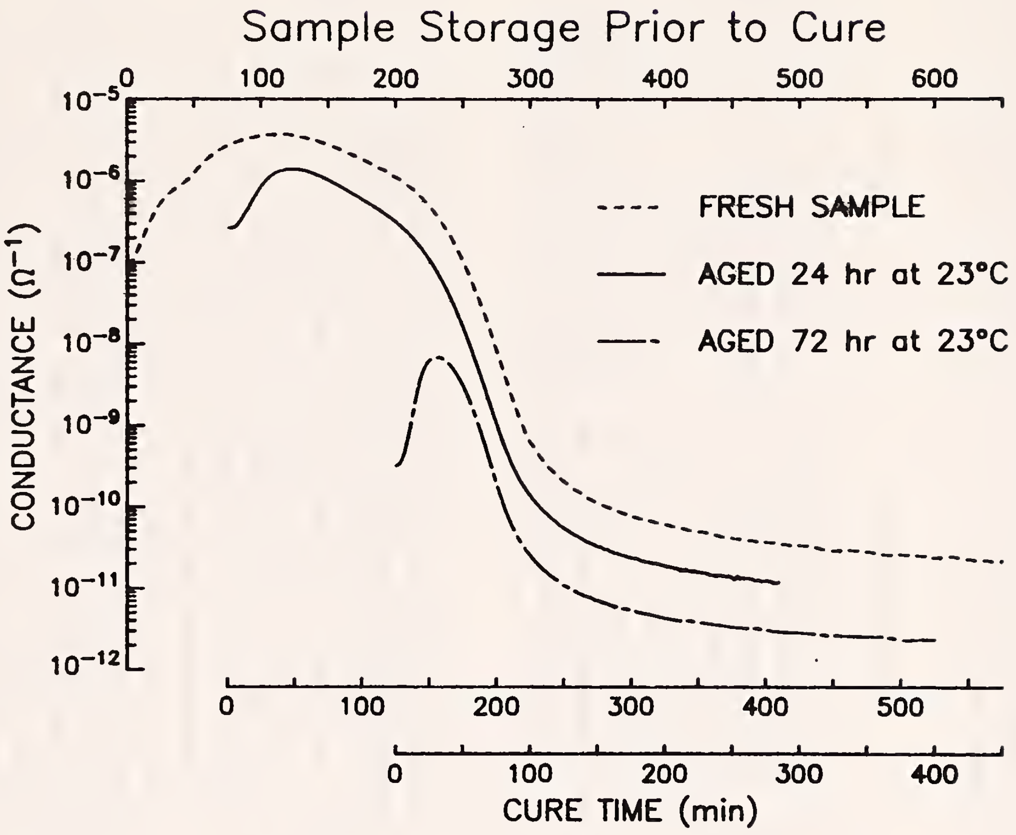

Figure 2: Conductance measurements of cure (at 55C) for samples of an epoxy-catalyst system aged before cure for various times at room temperature.

The discussion above describes a few of the comparisons that have been made in this task among the various cure monitoring techniques. The availability of this variety of measurement methods is a unique capability that will be exploited in the future. Although work on the development of new measurement methods and the improvement of existing techniques will continue, the major emphasis will now shift to the comparison of data from multiple techniques for simple materials. The focus will be on the selection and use of well characterized systems that exemplify the common cure mechanisms. A second area of work will be the development of models to describe and interrelate the cure monitoring results. Such models are necessary for process control and for data analysis since on-line monitoring will inevitably be limited to only one technique.

Investigation of Curing for Intaglio Ink

As an example of the practical applications of the techniques and expertise developed in the studies discussed above, one project in this task is developing measurement techniques to aid in the design, production, and use of intaglio inks. This work is in cooperation with the Bureau of Engraving and Printing (Department of Treasury).

Intaglio inks are complex mixtures of some ten ingredients. The dispersion of the solid phases in the liquid phase is critical to the cure behavior. A sedimentation technique using turbidity has been developed to monitor the break up and dispersion of the solid aggregates during the mixing and milling operations in ink production.

The size of the polymerizing resin molecules has a strong bearing on the rate of cure. In air-dry resin systems, oxygen in the air is a reactant. For small resin molecules, oxygen diffusion may be the factor limiting the rate of setting of the ink. Molecular size of oligomers and pre-polymers is conveniently measured with size exclusion chromatography (SEC). New SEC computer programs have been written for a laboratory computer systems. These programs characterize molecular size in terms of hydrodynamic volume, since the usual intaglio vehicle is a mixture of materials and therefore the molecular weight distribution cannot be determined. Newly procured materials can be compared automatically with previously procured batches. Changes in molecular size of polymerizing resins can be followed. These programs are being used to monitor ink cure in conjunction with tests which follow the viscosity of the curing ink as a function of time.

New water-soluble and water-dispersible electron-beam polymerizing resins are being synthesized from poly(ethylene glycol)/bisphenol A/acrylate sequences. The important parameters in terms of the cure behavior and properties of the resulting films are the viscosity of the resins, the molecular size, and the number of polymerizing groups per resin molecule.

Analysis of Structure in Polymers and Their Composites

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The determination of structure in thermoset resins and their composites is a vital step in relating processing and formulation parameters to performance. During the past year, neutron scattering was the main technique used to address the structure problem, and some of the results and progress will be described in this section.

Molecular Response to Large Strain Deformations

The molecular mechanisms associated with large deformations in crosslinked polymers has been a subject of extensive research. Most of these efforts, however, have concentrated on those materials with rather low crosslink densities such as rubbers. Neutron scattering has been the main research technique for determining the molecular response to the deformation process. The junctions within the crosslinked materials were found to deform following a scheme closely predicted by a phantom network model. For those materials of high crosslinking density such as epoxies, however, no experimental results about the changes in the molecular dimension have been reported using any direct measurement methods.

Based on our previous experience in the determination of the molecular network structure of epoxies using neutron scattering techniques, it is apparent that the epoxies composed of partially deuterated diglycidyl ether of Bisphenal A and difunctional amines of poly(propylene oxide) are the ideal candidates for the deformation study. The average distance between crosslinks can easily be calculated from the positions of the scattering peaks. As a result, a program along these lines has been initiated. All the specimens were deformed in the pure shear mode, and a pair of aluminum jigs were used to keep the specimens in their deformed state during the scattering measurements.

For those epoxies containing a 2000 molecular weight amine, the average distance between the crosslinks along the amine chain was found to be 4.3 nm and the distance along the epoxy link was 1.7 nm. The maximum amount of deformation before sample rupture was about 50%. Within this strain limit, the amine chains were found to elongate with the macroscopic strain. The amount of the stretch of the amines was far less than what is predicted by the junction affine model.

As the molecular weight of the amine decreased to 400, the average distance between the crosslinks along the amine decreased to about 1.7 nm while the distance along the epoxy chain was unchanged. For the low molecular weight amine, the maximum strain before sample failure was 30%. Surprisingly, within this strain limit, no change in the distance between crosslinks along either the amine or the epoxy chains was observed.
The glass transition temperature of the epoxy containing the low molecular weight amine was found to be 70C. In order to ensure that the molecules were

in equilibrium with the macroscopic strain, the following experiment was also conducted. While maintained in the deformed state the sample was heated to 90C, which was 20C above its glass transition temperature, for 20 minutes. The neutron scattering measurements were conducted on this deformed and heated specimen. Once again, the average distances between crosslinks within this deformed and heated sample remained identical to those in the undeformed specimens.

The above observation is striking and may also have important implications in a practical sense since most of the thermosetting resins used as composite matrices have distances between crosslink points that are less than those in the 400 molecular weight amine system. In light of this observation, the question that needs to be addressed is what parts of the molecular network are deformed in a specimen with a macroscopic strain up to 30% since major portions of the molecular network do not deform. There are at least two possible explanations for the above observation. The first is a defect-control model. This hypothesis would propose that the deformation is concentrated in some localized defect regions while major portions of the molecular network are located outside these defects. The analog of this defect model in metals or other crystalline materials is dislocation theory. The generation and movement of the dislocations accommodate the macroscopic strain while the lattice dimensions of the crystals remain unchanged. For this hypothesis, the unanswered question in the case of epoxies is the nature of the defects. A second possible explanation for the neutron results is that the deformation mechanism involves the unfolding of the molecular networks; however, the prerequisite for such a mechanism is that the average network within a bulk sample must be topologically two dimensional. In fact, this is true for the samples tested to date but would not be true for all epoxies. Experiments are now underway to elucidate the deformation mechanisms in greater detail. Amines and epoxies with different functionality and composition are included in this work to establish the generality of the findings.

Network Structure Revealed in a Solvent Swollen State

The molecular network structure of epoxy specimens made of protonated diglycidyl ether of Bisphenol A and linear diamines of poly(propylene oxide) were investigated using neutron scattering technique. Deuterated acetone was used to swell these epoxies to provide the scattering contrast. The molecular weight of the diamine was the experimental variable in the present work.

The swelling ratio as well as the scattering intensity in the small q (<0.18 A^{-1}) region for these epoxies were found to increase with the average molecular weight of the amines. Specimens were also prepared using two amines of different molecular weight, and found to be between the values obtained from the single amine containing specimens. A clear scattering maximum was observed only in the epoxy which contained the two amines of different molecular weights in equal mole ratio. This observation suggests the existence of a regular spacing between regions of different swelling ratios within an average molecular network.

A molecular model with a regularly alternating block structure was chosen to account for this observed maximum. A semi-quantitative comparison showed that the scattering data on an absolute scale agreed quite well with the theoretical result. The homogeneity of swelling, hence the homogeneity of the molecular network, has also been studied and compared successfully with the observed scattering intensities.

Relation Between Network Structure and Fracture Toughness

The fracture toughness is one of the major properties that needs to be enhanced for most thermoset resins. Composites using brittle resins as matrix materials are often susceptible to inter-laminar failure. The study of the molecular mechanisms of deformation in epoxies, as reported at the beginning of this section, is aimed at understanding the deformation processes which lead to fracture. In the present section, some of the preliminary results of our work on the relation between the fracture toughness and the network structure will be discussed.

For certain compositions, the toughness of the resins depends on the curing condition. For example, precuring the reaction mixtures at a temperature well below the glass transition temperature of the fully cured material followed by a normal cure procedure results in a tougher material for several formulations tested here. Such results have been observed in epoxies containing mixtures of 400 and 230 molecular weight amines. The network structures of the samples with different toughness but with identical composition were investigated using neutron scattering technique.

Deuterated acetone was chosen as the swelling agent. The swelling ratios for the samples with different toughness were found to be the same; however, a significant difference in the network structure manifested in the swelling process was revealed by the neutron scattering results. The correlation length calculated from the excess scattering intensity of the d-acetone swollen samples showed a strong dependence on the curing process. For materials subjected to a precuring cycle, hence with higher toughnesses, the correlation lengths were greater than those for the corresponding brittle samples.

One possible interpretation asserts that the excess scattering in the swollen epoxies originates from some network defects. The correlation lengths determined are then a measure of the size of these defects. This hypothesis suggests that the toughness of materials would be related to the size of the network defects. This conjecture is consistent with the results reported in the beginning of this section, namely, the deformation of the epoxies may be a defect-controlled process.

Performance of Polymers and Their Composites

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In studies of composite materials the measurement of performance properties is almost always a critical element. Consequently, the development of test methods and reference data is of great importance. During the last year, work in this area has focused in four areas: delamination, toughening mechanisms, characterization of tough resins, and fiber-matrix adhesion in composites. In most of the projects the objective was to understand the performance properties of the polymeric system in terms of the constituent properties and the processing/fabrication involved.

Delamination

In recent years, there has been a great deal of interest in composite delamination, i.e., the growth of cracks between layers of fibers either in the polymer that holds the fibers together or at the fiber-polymer interface. These cracks, which can grow from impact damage, substantially reduce the mechanical performance of a composite, particularly in compression. To design composites with more resistance to delamination, however, requires a better understanding of the failure processes involved and the factors that influence them. Previous work in the Composite Group has examined the relationship between delamination resistance and matrix resin toughness for a wide range of materials subjected to mode-I loading. A clear correlation was established, and the effects of other variables such as fiber-matrix adhesion were identified.

During the past year the mode-I results have been further refined with test results for a number of new systems. In addition, the studies were extended to include delamination tests in mode-II loading using the edge notched flexure specimen. As part of this effort, experiments were performed to examine the effects of the precracking method on the calculated fracture energy. This is important for the mode-II test because the crack growth is unstable. Different thickness shims were inserted into the specimen before fabrication to create precracks with known crack tip radii. In addition some specimens were wedged open to advance the crack beyond the insert, and thus create a sharp precrack. The fracture tests conducted on these specimens indicated that the sharp precracks gave the best results with the lowest fracture energies and least scatter. The blunt precracks not only gave high fracture energies, as would be expected based on previous work in this program and elsewhere, but also showed extremely wide scatter indicating a lack of reproducibility. Even the thinnest shim (5 μm) was found to be unacceptable. Consequently, only sharp cracks can be used to produce valid results in this test geometry.

These mode-II studies are now continuing with an examination of the correlation between fracture energies of various resins and their composites. As with other studies in the area, our preliminary results show increases in composite fracture energies for mode-II loading relative to mode-I loading, with the largest increases for the most brittle matrices. More systems must be examined, however, before a complete quantitative can be established.

Toughening Mechanisms

The generation of high fracture energy polymer systems for improved adhesives and composites is a major industrial goal. To assist this effort, basic studies of toughening mechanisms are being conducted in this subtask. A critical part of this work is the analysis of the deformation mechanisms present for toughened thermosets, and how these mechanisms relate to the morphology involved. Toughened thermosets are generally two phase systems consisting of an elastomeric phase dispersed as particles in a glassy thermoset phase. Properties such as toughness depend on the details of this morphology in ways that are, at present, only vaguely known.

As part of this program, an electron microscope technique for the analysis of morphology was developed by A. J. Kinloch (Imperial College) and applied to characterize a variety of systems whose fracture properties were also studied. The results show that the fracture behavior could not be correlated in a unique way with the volume fraction of the elastomeric phase as had been proposed previously in the literature. The major problem with such a correlation is that the fracture energies are loading rate and temperature dependent, and so different relationships are obtained for different test conditions. By using a simple viscoelastic approach, the rate and temperature dependence could be modeled for each material tested with an empirical equation whose parameters are then material constants independent of test conditions. Even these parameters, however, could not be correlated with volume fraction alone. In fact, samples with different distributions of elastomer particle sizes but similar volume fractions gave quite different fracture properties. Consequently, a simple comparison based on volume fraction will not correlate results for different morphologies, and thus more study is needed before meaningful relationships can be established.

Fracture Properties of Tough Composite Matrix Materials

Future composite materials will use tough matrix resins such as rubber modified epoxies among the thermosets and poly (aryl ether ether ketone) (PEEK) among the thermoplastics. These matrix materials improve the performance of the composite particularly with regard to the delamination problem discussed above. However, the quantitative evaluation of resistance to crack growth in bulk resin samples is difficult for such very tough polymers. Since they are non-linear materials whose deformation involves plasticity and non-linear viscoelasticity, the customary means of linear elastic fracture mechanics do not work very well. One possible way of characterizing such materials is by the use of the so-called J-integral. The J-integral may be described as the force on a crack and the deformation zone around it, and has been shown to apply rigorously to non-linear elastic materials. It can be measured by determining the energy required to advance a crack, and has been successfully used to characterize the resistance to crack growth of tough steels.

An experimental program to use J-integral methods for determining the fracture resistance of tough polymer composite matrix materials has been initiated. The first work will be on rubber modified epoxies with possible subsequent extension to thermosets.

Fiber-Matrix Bonding in Polymer Composites

Thermoplastic polymers offer great promise as composite matrix materials because of their superior toughness, high temperature performance, and ease of fabrication. As reported last year, however, delamination studies of carbon fiber reinforced thermoplastics conducted in this program have shown poor fiber-matrix bonding, and this prevents them from achieving the full potential, particularly in load-bearing applications where delamination is a problem. Consequently, there is a need to improve the adhesion between fibers and thermoplastics.

In the case of carbon fiber reinforced epoxies, it has often been found beneficial to precoat the fibers with an epoxy prepolymer (called asizing) in order to improve bonding in the composite. In the same way, it may be postulated that appropriate coatings might improve the performance of thermoplastic composites. Currently at NBS studies are underway to determine the effect of polymer and metal coatings on the adhesion of carbon fibers to thermoplastic materials. Polymer coatings are being applied by vapor phase polymerization (through cooperation with scientists at the Naval Research Laboratory) and by electrodeposition from monomer solutions, while metal coatings are being applied by scientists in the Metallurgy Division using an electroless process. After a careful study of all established tests to evaluate fiber-matrix bonding, the "critical length" measurement was selected. In this test a single fiber is embedded in a coupon of the desired resin, and the coupon is then stretched parallel to the fiber axis causing the fiber to break into ever shorter length segments. Eventually the segment lengths become too short to transfer sufficient load into the fiber to cause rupture. This minimum length, or parameters derived from it, provide a measure of the fiber-matrix bonding. In the initial experiments this technique was used to evaluate epoxy coupons with coated and uncoated fibers. This provides an important test to determine if the coatings decreased the already good adhesion normally found with epoxies. Some early results for studies with each of the coatings is given below. Work planned for the future will extend these experiments to thermoplastic resins.

Carbon fibers, coated by vapor-phase polymerization of butene, were examined first. It was found that the coated fibers adhered about as well to the resin as uncoated fibers. There was however a greater scatter in critical lengths which could indicate some damage to the fibers resulted from the coating process. If so, this would complicate the interpretation of the results. Experiments to independently measure the strengths for coated and uncoated fibers are now underway.

Carbon fibers coated with Cu and Ni films have also been studied with the critical length test. The results suggest that the bonding with the coated fibers was not dramatically inferior to that for the uncoated fibers. The failure mechanism was different, however, in that fiber appears to break while the coating does not. This limits the accuracy of the comparison with uncoated fibers, and may suggest that the coating-fiber bond could be improved. Further work is planned with coatings that scientists in the Metallurgy Division believe will give better adhesion to the fiber.

Experiments were also conducted on carbon fibers coated by electropolymerization of ruthenium ion-labelled 4-vinyl pyridine. One reason for selecting this material is the ability to characterize certain aspects of the coating by electrochemistry using the ruthernium. The polymer was grown onto the fibers by a slow current-cycling process, in an effort to produce a uniform coating and maximize adhesion to the carbon surface. Identification of the polymer was made by comparison of its FTIR spectrum to that of a similarly grown coating on a flat platinum surface where the coating could be identified by other analytical techniques. Preliminary critical length measurements in epoxy resin have clearly shown that the bonding was not decreased by the coating.

POLYMER BLENDS

Approximately 15 to 20% of the estimated 47 billion pounds of plastics to be produced in the United States during 1986 will be polymer blends. In the same way that stainless steels are alloys of iron, chromium, and nickel to make metal resistant to corrosion, polymer blends are a mixture of two or more polymers to create plastic alloys with new properties. Mechanical properties, flame retardance, processability, as well as many other polymer properties can be improved by blending.

While the blending of low cost polymers is a relatively inexpensive way to produce materials with new properties, most polymers fail to form a homogeneous phase during the blending process. In a majority of instances, the heterogeneous blend has poorer mechanical properties, but in a small number of cases large and favorable synergistic effects are obtained. For example, the impact resistance (toughness) of a heterogeneous polymer can sometimes be increased by an order of magnitude whereas such synergism is never observed in a homogenous blend. The properties of a heterogeneous blend are dependent on the details of the microstructure and interfacial tension between phases. The key to understanding how to produce desirable heterogeneous blends is a better knowledge of the fundamental factors that control the blend morphology, interfacial adhesion and the relationship between the kinetics (rates of separation) and the thermodynamics (static properties) of polymer blends.

Two research techniques, small angle neutron scattering (SANS) and temperature-jump light scattering (TJLS), are being used to obtain basic information for predicting the conditions under which polymers are miscible and therefore will form a homogeneous phase and for controlling the rate of demixing and the size of phase separated microdomains if the polymers are immiscible. These methods allow phase diagrams to be determined and the phase separation kinetics to be studied. In addition to these two methods, Forced Rayleigh scattering (FRS), small-angle X-ray scattering (SAXS), and electron microscopy are also used in polymer-blend studies.

FY 86 Significant Accomplishments

- The molecular weight dependence of the binary interaction parameter, χ, has been obtained for polystyrene/poly(vinylmethylether) blends using small angle neutron scattering. This has been used in conjunction with a temperature jump light scattering technique to obtain the mutual diffusion coefficient of this polymer blend system above and below the critical point. The critical slowing down, and the analytical continuity of free energy and diffusivity have been demonstrated quantitatively for the first time.

- Blends of poly(vinylidene fluoride) (PVF_2) and poly(ethylacrylate) have been used in their compatible region to study the crystallization process and morphology of PVF_2. The structures formed evolve from single crystal lamellae to more complex aggregates and eventually to spherulites. The morphology has been studied as a function of PVF_2 concentration.

- A theory for the dynamics of phase separation of block copolymers into ordered lamellar microdomains has been developed. The time dependence of the scattering function after the system is quenched into the microphase spinodal region has been calculated. The similarities and differences between block copolymers and binary blend systems have been analyzed.

Experimental

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J. Clark, Y. Matsushita[1]. T. Sato[2], Q. Tran-Cong[3], Pei Sung[4],
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Experimental Study of Thermal Fluctuations in the Spinodal Decomposition of Polymer Blends

The kinetics of spinodal decomposition of a binary polymer system of polystyrene/poly(vinylmethylether) near its critical composition has been studied by the temperature jump light scattering technique. The results indicate that the linearized theory of the Cahn-Hilliard-Cook type which includes the thermal fluctuation term describes the polymer system very well in the early-time and shallow-quench region. The virtual structure factor, $S_x(q)$, which is a consequence of including the thermal fluctuations, has been obtained for the first time. For experiments of deeper quench, the virtual structure factor becomes small in our experimental q range, and the time dependent static structure factor, S(q,t), reduces to the original Cahn-Hilliard type.

Application of a Photodimerizable Probe to the Forced Rayleigh Scattering Technique for Measurement of Self-Diffusion of Polymer Chains

A new type of photochromic compound, a bis-9-anthryl methyl ether (BAME), is introduced as a potential probe for the Forced Rayleigh Scattering (FRS) technique. Upon irradiation with U.V. light ($\simeq$ 360 nm), BAME undergoes intramolecular dimerization which involves a large refractive index change in the visible region. The dimerization process is known to be essentially irreversible in the absence of short U.V. ($\simeq$ 250 nm) light at room temperatures and above. A derivative of BAME is synthesized and chemically attached to polystyrene chains. Some photochemical properties of the BAME labeled polystyrene have been reported together with the results of a preliminary diffusion measurement of polystyrene by the FRS technique.

Structure and Morphology of MDI/BDO Based Polyurethane Materials

Polyurethanes are random block copolymers consisting of alternating sequences of hard and soft segments of variable length along the chain. The hard and soft segments separate to form hard and soft segment domains. In the case of copolymers containing less than about 50% hard segments the hard segment domains act as physical crosslinks for the soft segment matrix. The size, shape and structure of these hard segment domains are believed to play a crucial role in determining the physical properties of such polyurethanes. We have begun work, in cooperation with the Food and Drug Administration, on characterizing the hard segment morphology of a series of polyurethanes based on 4'4'-diphenylmethane diisocyanate (MDI) and 1,4-butanediol (BDO) as the hard segment. These polyurethanes are important as insulating materials for pacemakers as well as other biomedical applications. Initial work has indicated that the polyurethanes in the as-received state are only poorly microphase separated. This was determined by small angle x-ray scattering and electron microscopy. An increase in phase separation can be observed after annealing at elevated temperatures (140 °C) or after soaking in acetone. Future work will examine the time dependence of the change in the phase separation during annealing. In addition, Wide Angle X-ray Scattering (WAXS) has been used to study the changes in morphology with deformation. Unlike most semicrystalline polymers, the MDI/BDO repeat unit undergoes a chain conformation rearrangement from a contracted form to the fully extended form on deformation. In addition, WAXS indicates that the transition between the two chain conformations (each of which exhibits a distinct crystal structure in annealed samples) is continuous with the d-spacing associated with the monomer repeat units shifting continuously to lower angles (larger d-spacing values) with increasing deformation.

The Morphology of Blends of Poly(vinylidene Fluoride) and Poly(ethyl acrylate)

In the previous year we performed extensive cloud point and melting point temperature measurements in order to determine the phase diagram for this system. This year we have characterized the morphology of PVF_2 crystallized from blends in the composition range where the melt is compatible (single phase). Crystallization experiments were done as a function of temperature and composition. As the PVF_2 concentration increases from 0.5 wt% to 15wt% the structures formed evolve from single crystal lamellae to more complex aggregates, and eventually to spherulites. The phenomenon of twisting of lamellae, begins to appear in blends at about 5wt% PVF_2 crystallized at 150 °C. In blends containing 15wt% PVF_2 crystallized at 150 °C where distinct spherulites are formed, periodic branching of the lamellae along the radial growth direction of the spherulite is observed. This branching has the same period as the lamellar twist observed in the spherulites with polarized light.

Future work will involve studying the small angle x-ray scattering of the single phase melt as a function of temperature as the cloud point is approached in order to measure the correlation length and, possibly, the interaction parameter, χ.

Theory

E. A. Di Marzio, P. Van der Schoot[1], R. J. Rubin, I. C. Sanchez, F. L. McCrackin, M. Olvera de la Cruz, J. A. Marqusee, E. Passaglia, C. M. Guttman and M. Mansfield[2]

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Glass Temperature of Polymer Rings

The glass temperature T_g of a bulk polymer consisting of polymer rings has been predicted using the Gibbs-Di Marzio theory of glasses. The predictions were found to be in accord with experimental data of S.J. Clarson, K. Dodgson and J.A. Semlyen (Polymer 26, 930 (1985)). An interesting feature is that T_g of rings rises as we lower the temperature. This is opposite to the behavior for linear systems. It is now possible by mixing linear and ring systems to have a polymer blend whose glass temperature is independent of molecular weight.

Estimation of the Amount of Adjacent Reentry in Polymer Crystallization

We have developed a treatment of polymer chain folded crystallization in which stems are incorporated into the crystal by both adjacent and non-adjacent reentry. By defining certain stages of partial incorporation of a molecule as separate species, we have been able to adapt a kinetic transfer matrix technique derived previously to solve the problem of the growth of multi-component chains to the solution of the present problem. A prescription is given for obtaining the relative amounts of adjacent and non-adjacent reentry as a function of the forward and backward rate constants for stem incorporation. The difficult problem of determining the rate constants as well as the actual numerical calculations are also being addressed.

Models of the Crystal-amorphous Interface

The presence of a surface near a polymer molecule is shown to invalidate the concept of universality. It is shown that one cannot scale the properties of polymers near a surface. One is forced to use molecular models for the loops of segments near a surface. Previous lattice model results are shown to retain their validity. In particular, the bound of 2/3 for the amount of tight folding is shown to be valid.

Spatially Dependent Orientational Packing Entropy

The orientation dependent packing entropy near a surface has been previously calculated only for the case of non-spatially varying density and orientation. Experimental data however show that orientation is a function of depth in membranes. An attempt is being made to determine if these orientation effects can be incorporated into pre-existing lattice models, such as the very successful Sheutjens-Fleer treatment. The basic formulae for orientation dependent probabilities of stepping between adjacent lattice sites have been obtained and a minimization procedure for determining their actual values is being formulated.

The Dimensions of Block Copolymers

A diblock copolymer has a thickness which varies as the 2/3rds power of the molecular weight. The original treatment which obtained this law is generalized by incorporating the entropy of packing for ordered systems (the 2/3rds law implies that the molecules are stretched perpendicular to the lamellar surfaces and therefore ordered.) It is found that the dimensions can vary from the 2/3rds to the first power of the molecular weight.

Diffusion-Controlled Rates of Relaxation and of Chemical Reaction [Work Undertaken in Internal Sabbatical Program in Collaboration with Members of the Thermophysics Division, 774]

This sabbatical program was devoted to the study, in model systems, of: 1) the concentration dependence of the rate of diffusion-controlled reactions, and 2) the diffusion-controlled rate of relaxation in the presence of traps. Among problems of current interest which fall in these categories are: growth of colloidal or aerosol particles, precipitation, catalysis, fluorescence quenching, combustion of fuel droplets, and transport and relaxation processes in disordered materials.

Two related investigations in the area of diffusion-limited reactions have been carried out.

A) Lattice model simulations in one- and two-dimensions of random-walking chemically reacting species in the presence (and in the absence) of traps have been carried out in collaboration with J. Hubbard, J. Rasaiah, and S.-H. Lee. A mean field theory solution of the nonlinear reaction equations has been developed which can qualitatively account for the results of the numerical model simulations.

B) A one-dimensional discrete lattice model of diffusion-limited chemical reaction has been treated exactly. Our solution is analogous to that obtained by D.C. Torney and H.M. McConnell in the continuum limit. Exact results for the discrete lattice model serve as bench marks for the numerical simulations in A).

Computer Simulation of Phase Changes in Polymer Solutions

A polymer solution is simulated by many excluded volume chains on a cubic lattice. The effect of temperature is simulated by varying the attractive energy between the segments of the chains. The changes of the radii of gyration, mean-square end-to-end distance and diffusion coefficient with temperature and concentration of the solution has been calculated. The change of clustering size of polymer chains with temperature has been observed. These calculations will be extended to the case of two types of chains to represent blends and possibly to the case of copolymers.

Chain Configurations in Lamellar Semicrystalline Interphases

The nature of chain configurations at the crystal/amorphous interface of semicrystalline polymeric materials is not yet well understood. A lattice theory has been developed which allows one to predict the degree of adjacent reentry, the orientational order parameter and the mean lengths and types of amorphous configurations. The theory permits systematic levels of approximation for correlations among neighboring bonds along the chains subject to the interfacial constraints. For freely flexible chains, a sharp interphase is found with approximately 73% of the chains which emerge from the crystal reentering at sites which are immediately adjacent. The mean lengths of amorphous walks and loops are found to be significantly longer than predicted by random walk statistics. These predictions agree with recent Monte Carlo simulations.

Coagulation and Late Stage Phase Separation

A simulation and analysis of a one-dimensional coagulating system has been performed. Since coagulation of droplets is an important mechanism for coarsening in phase separation, we have determined what features of binary phase separation are exhibited by a system whose dynamics are governed solely by coagulation. We find the droplet size grows as $t^{1/3}$ and the scattering function develops a well defined peak which grows in intensity and shifts to smaller wavevectors with time. Furthermore, the scattering function is shown to have a scaling or self-similar form which is also characteristic of late stage spinodal decomposition. The droplet size distribution is also shown to obey a scaling relation. These results are explained by mean field type arguments.

Microphase Separation Dynamics

Block copolymers microphase separate into ordered domains of the size of the radius of gyration of the polymer. A theory for the dynamics of the formation of lamellar domains from the disordered state is being developed. The scattering function in the disordered phase has a broad peak which upon quenching into the microphase spinodal region grows exponentially in time and then plateaus to its new equilibrium value. Contrary to the case of binary phase separation, no shift in the peak position is seen. For shallow quenches the dynamics is dominated by fluctuations with wavevectors corresponding to the maximum in the scattering function. Using a Landau expansion of the free energy, the time dependence of the scattering function is determined in the linear region (exponential growth) and the non-linear region (plateauing) for this microphase separation.

SAXS and Pole Figure Facilities

J. D. Barnes and L. Ouzts

Small Angle X-ray Scattering Camera

The 10 meter small angle X-Ray camera is being used in a "breadboard" configuration. Under the guidance of Dr. Chris Vonk we have calculated all of the parameters for a three pinhole design to minimize parasitic scattering. The major beam path elements have been fabricated and installed, except for the beam stop mount and the beam monitor mount. Some experimentation is needed to establish the optimum geometry for the monitor detector, scatterer, beam combination.

Additional beam path components which have not yet been designed or purchased include an Fe-55 source for checking uniformity of detector response, the automatic sample changer, and a suitable automatic inserter for the Fe-55 source. These will be completed as early as possible in FY 87.

Initial Operation

Small angle scattering images have been obtained. These indicate that there is adequate intensity and resolution for operation of the system at a resolution of 1000 angstroms. Dr. Fred Mopsik has assisted us with a comprehensive evaluation of the noise characteristics of the detector. The grounding of the circuit elements in the detector was reworked to minimize pickup due to ground loops. This improved the detector resolution noticeably. We have devised and tested procedures for calibrating the positional response of the detector and we have found this to be adequate and reliable. We are working on calibrating the detector sensitivity as a function of image position. We have observed minor amounts of non-uniformity that may be attributable to non-uniformity of wire spacing in the cathode planes. These effects do not interfere with qualitative interpretation of the data, but they are important for quantitative work.

Polymers Division staff are being encouraged to prepare specimens and use the camera. There are a number of specimens of anisotropic semicrystalline polymers, polymer networks, copolymers, and polymer blends that are awaiting evaluation.

Operation As A User Facility

Operation as a full-scale user facility is dependent upon completing the automatic controls for the beam path, including safety interlocks for detector protection, automatic beam stop positioning, and automatic sample changing. The primary problems in this area involve computer interfacing and software development.

X-Ray Generator Upgrade

We have procured a turbomolecular vacuum pump for use with the Rigaku Denki 12 kW generator. Installation will be done in early FY 1987. This upgrade will allow the generator to operate with a cleaner vacuum, which should increase reliability at high power levels.

X-ray Pole Figure Facility - Interest From Outside NBS

The software developed for orientation measurements by NBS has been provided to workers at the Army Materials Research Command and the University of Dayton Polymer Research Institute. Graduate students from Washington University and workers from Picatinny Arsenal also made use of the facility during FY 1986.

DENTAL AND MEDICAL MATERIALS

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

Materials-research efforts are aimed at development of materials and techniques for promoting adhesion of restorative materials to tooth dentin and enamel. Novel approaches 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 as are methods for improving properties of surgical bone cement such as durability, radiopacity, and coupling between the bone-metallic implant system. New tissue adhesives are being explored. Testing of retrieved biodegradable bone plates was conducted. Studies of calcium phosphate compounds for endodontic sealants, bone augmentation, or caries-reducing agents are being investigated. The basic chemistry of precipitation of calcium phosphates is explored as it relates to formation of mineral deposits such as bone, teeth; and atherosclerotic plaque is also under investigation.

Theoretical and experimental studies of stresses within bonded dental systems are explored with the objectives of defining the most compatible material-property combinations and geometric designs for porcelain-to-metal, tooth-to-resin, resin-to-filler bonding and so forth.

Techniques for characterizing casting processes and effects of variables including alloy compositions are being studied with a view toward improved alloys and processing methods.

FY 86 Significant Accomplishments

- A promising procedure has been developed for bonding to bone. An isocyanate containing copolymeric liquid provides a stronger, more permanent, water-resistant material than other bone adhesives.

- Dental crowns cast from pure titanium have been placed in several patients in an ongoing clinical study. Methods to achieve greater dimensional accuracy in these castings are being explored with emphasis on compounds that produce a permanent expansion of the investment mold material.

- Tests of retrieved fiber reinforced-biodegradable implant bone plates for the U.S. Army Institute for Dental Research showed significant deterioration in mechanical properties within two days of implantation. The results pointed to directions to be taken for improved performance.

- Flexible prepolymer monomers and bulky diluent monomers (based on vinyl thermosetting silyl ethers) were synthesized that yield high filler content dental composites with reduced water uptake, adequate mechanical strength, and excellent esthetics.

- The susceptibility of glass ionomer cements to brittle fracture and degradation under acidic conditions has been reduced by the incorporation of water-soluble or water compatible vinyl resin systems.

- Interfacial bonding of dental composites in the presence of water has been enhanced by the use of a newly synthesized multifunctional silane coupling agent.

Dental Composite and Cement Sealant and Adhesion Chemistry

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Vinyl-based thermosetting composites, are increasingly used in stress-bearing applications traditionally reserved for amalgam fillings. However, they are deficient in wear resistance, color stability and margin adaptability. The oral environmental resistance (OER) of polymer-based dental materials is a significant factor in determining their in vivo performance. To enhance the OER two complementary approaches are being pursued. One is to increase the degree of polymerization and crosslink density by the synthesis and formulation of flexible, multifunctional methacrylates (e.g., silicon-containing monomers) and flexible chain transfer agents (e.g., polythiols). The other approach involves designing resin systems that have low solubility parameters. We have synthesized and formulated resin systems that yield composites containing significant amounts of fluorocarbon or siloxane segments in the matrix phase and still have acceptable mechanical properties. Composites using a siloxane-containing resin showed improved OER and acceptable strength. Emphasis also is directed to monomer systems that have minimal (preferably zero or slightly positive) changes in volume on polymerization and that have rheological properties that permit high filler loadings. A novel type of dental resin system was formulated based on recently synthesized silyl ether derivatives of BIS-GMA. These silyl ether multifunctional methacrylates have both low viscosity and excellent wetting characteristics which lend themselves to the preparation of composites of high filler content. Composites with adequate strength, excellent esthetics and low water sorption were formulated using these silyl ether monomers. The long-term hydrolytic stability and potential for "self-healing" of these unique types of matrices are under investigation.

A series of spiro orthocarbonate monomers which undergo free radical, double ring-opening polymerization with expansion in volume has been synthesized. By varying the degree and pattern of substitution, the melting points of the spiro monomers and the mechanical properties of the resulting polymers can be tailored to meet different formulation requirements. When applied to dental composites, the incorporation of spiro monomers into conventional dental resins yielded composites which exhibited a 30 percent decrease in polymerization shrinkage along with a 250 percent increase in micromechanical retentive adhesive strength.

A major deficiency of dental composites, is their less than optimal interfacial bonding phase which also may contribute to their relatively low service life in aggressive environments such as the mouth. A study of different types of silane agents and techniques, led to the following conclusions: (1) For silane agent types, the order of increased bonding effectiveness is methacryl > mercapto > dimethylamino. (2) Integral blending, which aids in filler loading, is not as effective as presilanization. (3) Dual silanization techniques utilizing both integral blending and presilanization appears to be the most effective method of promoting interfacial bonding. (4) The tranverse strength test is a more sensitive test for evaluating interfacial bonding than the diametral tensile strength test. (5) A newly synthesized multifunctional silane coupling agent, having increased potential for bonding to both the matrix and siliceous filler as well as the capability of forming a more hydrophobic polysiloxane, yielded composites with enhanced hydrolytic stability.

Another objective of this subtask has been to synthesize specific monomers or oligomers and to prepare suitable formulations using these compounds as ingredients in adhesives to bond to dentin in an aqueous environment. Thus, the dimethacrylate ester of 5-(2,5-dioxotetrahydrofuryl)-3-methyl-3-cyclohexene-1,2-dicarboxylic acid as well as a series of oligomers of isocyanatoethyl methacrylate (IEM) or m-isopropenyl-α,α-dimethylbenzyl isocyanate (TMI) with ethyl acrylate, butyl methacrylate or hydroxyethyl methacrylate (HEMA) were synthesized. The urethane methacrylate of IEM or TMI with HEMA were also prepared. The isocyanato containing monomers or oligomers reacted with bone, but only slowly with dentin. However, glutaraldehyde treated dentin bonded strongly to dental composites using these isocyanato containing oligomers. The bond strength obtained was of the same magnitude as that obtained with ferric oxalate, a surface active agent and a diadduct of HEMA and pyromellitc anhydride (see below) or with glutaraldehyde-HEMA treated dentin. The composition of the monomeric ingredients can be easily modified to provide relatively high molecular weight compounds with low volatility. A low rate of diffusion into tissues by these adhesives is expected to result in a low degree of toxicity. The biocompatibility will have to be established.

Non-eugenol containing dental cements based on vanillate or syringate esters, o-ethoxybenzoic acid (EBA) and zinc oxide, have been developed in this laboratory. These materials do not dissolve in an aqueous environment and have superior mechanical and adhesive properties compared to presently used cements. Extensive studies conducted recently have shown the biocompatibility of these luting agents to be equal to or better than that of commercial cements. Limited clinical studies to determine their effectiveness have been initiated elsewhere. Toxicological investigations of modified formulations (containing acrylic monomers) for temporary fillings are underway at three universities.

The feasibility of utilizing halato polymers derived from the acid-base reaction dimer acid (DA) and trimer acid (TA) with various inorganic bases as dental cements has been established. (See Polymers Division Report for 1985.) Hybrid composite cements with enhanced mechanical strength can be formulated using a variety of dental resins and initiator systems.

A thin layer of cement is used for the complete closure of the margin of crowns and inlays and for retention of the restoration. Film thickness (FT) and retention of zinc phosphate, polycarboxylate and ionomer cements were determined as a function of power-liquid (P/L) ratio. The relationship between FT or P/L ratio and retention is complex and depended on the type and brand of cement. Venting lowered FT and increased retention. Results should assist in developing improved techniques for placing inlays or cast crowns.

Previous studies showed that acidified aqueous solutions of ferric oxalate, a surface-active compound, and a dimethacrylate coupling agent prepared tooth surfaces for strong adhesive bonding with dental composite resins. The bond strength obtained are much greater than those possible with present commercial products and may eliminate the need to cut away healthy dentin for mechanical retention of esthetic filling materials. Laboratory studies have shown that aluminum oxalate can be substituted for ferric oxalate, with potential improvements in color stability in vital teeth. Biocompatibility studies of the simplified aluminum oxalate system are underway.

A new activity is the development of inserts for composite restorations. The development of esthetic inserts may be a means to overcome deficiencies with composites. Prototypic inserts have been developed and used in cavities in extracted teeth. Another new activity is designed to develop polymeric protective coatings for tooth crown and root surfaces. These coatings must have durable adhesive bonding to both enamel and dentin, and recent discoveries have been promising. Patents are pending on some of the innovations just described.

Recent experiments on diametral tensile test specimens of dental composites have failed to reproduce evidence of a size effect in accord with Weibull Failure Statistics. Our best explanation for this negative result is that the polymerization reaction is very sensitive to temperature and that the temperature rise due to the exothermic polymerization can be expected to be quite different in the different sized specimens.

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

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Wear measurements have been extended to include glass-ionomer cements. Glass ionomer cements are noted for their adhesion to tooth structure. They also are noted for their propensity toward brittle fracture and for their erodible nature especially in acidic environments. One approach to ameliorating the excessive brittle nature of the glass ionomer cement is to incorporate a water soluble, somewhat flexible vinyl resin capable of blending with, or even interpenetrating, the glass ionomer network during the dual curing process. Using an aqueous, compatible, free radical initiator system (e.g., hydrogen peroxide and ascorbic acid) with a water soluble monomer such as 2-hydroxyethyl methacrylate, hybrid cement composites were prepared which not only have a "rubber toughened" nature as evidenced by their improved diametral tensile strength and resistance to catastrophic failure but exhibit greater resistance to acidic penetrants.

Castings of titanium crowns have been made for dental patients and are being observed periodically for wear of the opposing tooth and the Titanium as well as for other subjective responses. It is too early to determine if wear on the opposing tooth is significant.

In vitro tests are continuing for microleakage at composite-tooth interfaces. The method of application and the techniques for placing various materials are being studied in order to be able to advise dentists on the preferred techniques.

Investigation was completed on the reduction of dentinal hypersensitivity by means of an clinical hydroxy apatite precipitating paste.

Composite restorations with enhanced polymerization were retrieved following clinical testing and were evaluated and assessed with low power microscopy. Results showed that the wear was virtually indistinguishable from the controls. This may be due to a factor which could off set the expected enhanced durability, i.e., additional polymerization shrinkage may have made margins more susceptible to failure because of an increased marginal gap.

Dental Alloys, Ceramics, Metrology, and Analysis

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Research on the effects of investments on the casting of dental alloys continued. It was found that batch variations of the same investment affect only the magnitude of the castability value, C_v. (See Polymers Division Report for 1985) and the temperature dependence is unaffected. Each brand of investment produces different magnitudes and temperature dependence of C_v for a given alloy composition. A surface and chemical analysis of investment patterns is under way.

A two dimension finite element program was developed for evaluating residual stress in dental porcelain. This program allows for variable cooling rates.

It also incorporates the effects of cooling rate on the glass transition temperature, and the effects of temperature on the elastic modulus, shear viscosity and coefficient of thermal expansion of porcelain, as well as evaluating the temperature distribution during cooling. Results are being analyzed, but at this point it can be stated that the incorporation of a temperature-dependent elastic modulus affects the results to only about one percent.

Work is continuing on exploring various ways to inpart a permanent expansion to the investment mold materials which are used in casting titanium dental appliances. A proprietary mold expander that has been partially successful for this purpose was identified at NBS as the mineral "kyanite". Kyanite is an inexpensive and abundant aluminum silicate (Al_2SiO_5) which occurs in nature as a metastable high-pressure phase. When heated to 1400 °C it begins to decompose into the equilibrium phases (Mullite plus Silica) and this transformation is accompanied by a density decrease of about 20 percent. Experiments are now under way to develop a better understanding of the firing reactions and to find ways of inhibiting the shrinkage and simultaneously retarding the tendency toward cracking of the mold which also limits the effectiveness of the expander. The initial experiments on setting expansion of dental casting investments with multidirectional strain gauges were completed.

Two computer facilities were installed for the group; one is a terminal that is connected to the Cyber facility through the NBS net. This facility has been used principally for finite element analysis of porcelain-fused-to-metal systems. The other is an IBM PCAT which is being used principally for data reduction and for the analysis of Weibull fracture statistics. By analyzing samples taken randomly from known Weibull distributions, it is now possible to evaluate the confidence intervals for the estimates of parameters for PFM and other experimental samples. Parameters can be estimated for both two and three parameter Weibull distributions by maximum likelihood techniques. The resulting data can be plotted along with the best fitting distribution function.

Calcium Phosphate Chemistry, Biochemistry, Structure and Clinical Implications

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A ultramicro analysis system developed in this laboratory specifically for oral research has been used to study the degree of saturation of human enamel mineral in plaque samples recovered from individual tooth sites. The results of this study indicates that human dental plaque, in the absence of sucrose or other food substances, is supersaturated with respect to all pure calcium and phosphate phases. This demonstrates the existence in plaque fluid of substances which prevent crystallization or restrict crystal growth. There is no trend in the data which would account for the known site, specificity of caries.

A calcium phosphate cement development during the previous report period was evaluated both morphologicaly and functionally in vivo using a rat tibial implantation model. Both prefabricated and paste forms of the cement were used for bone implantation. Preliminary data provided an attractive biological profile for this new material which includes (1) no systemic toxicity, (2) no inflammatory response, (3) no foreign body response, (4) good dimensional stability of the implant, and (5) evidence of soft tissue and bone ingrowth into the voids in the material.

Application of $CaHPO_4 \cdot 2H_2O$ (DCPD)-forming solutions has been shown to increase substantially the enamel reactivity toward fluoride (F). The effectiveness of a variation of this treatment procedure, in which the DCPD-forming solution was replaced by a viscous carboxymethylcellulose gel containing monocalcium phosphate monohydrate (MCPM), was evaluated using extracted human molars. The MCPM gel has advantages over the DCPD-forming solution because the treatment agent can readily be delivered to specific sites where the tooth needs the protection most.

Several mathematical models have been proposed to describe the diffusion process during caries lesion progression. A study in which a diffusion cell comprising two compartments separated by a membrane of known ion permselectivity was used as an experimental model to study how the dynamics of diffusion affect dissolution and precipitation of hydroxyapatite and other sparingly soluble calcium phosphates. The results suggest that the rate of caries progression may be significantly reduced by making the tooth surface highly anion permselective.

There is growing evidence that biomembranes play an important role in initiating and/or controlling mineral deposition during the early states of calcification in such vertebrate hard tissues as cartilage, dentin, and bone. In particular, the first mineral crystals formed in these tissues are often associated with the membrane surfaces of submicron size, extracellular structures known as matrix vesicles. Synthetic lipid vesicles (liposomes) previously developed by us as models for studying matrix vesicle calcification were employed during the period covered by this report to investigate the role that various biomolecules found in matrix vesicle membranes may be in regulating this type of biomineralization. The membrane biomolecules most extensively investigated to date have been the acidic phospholipids, phosphatidic acid and phosphatidylsevine. Results suggest that their function in vivo is to control rather than to initiate mineral deposition processes in matrix vesicles.

The manner in which precipitation was initiated played a crucial role in determining the size apatite crystals can attain in physiological-like solutions. Crystals formed by seeded growth were much larger than crystals formed in spontaneously precipitated reactions. The data suggest that the formation of amorphous precursor phases, may be a more critical factor in delimiting crystal size than such solution conditions as the degree of supersaturation.

High resolution microradiographics of "dental specimens" of various thicknesses were also investigated using synchrotron radiation from the NBS Material Science beamline x-23A, National Synchrotron Light Source at Brookhaven. Results from these studies indicate that this technique has promise of allowing one to follow the structural changes accompanying the formation, demineralization and remineralization of hard tissues in realtime or quasi realtime.

The calcium phosphate solubility properties in serum and the nature of the mineral phases in cardiovascular plaques are being investigated. The combination of data from these two sources clearly indicates that octacalcium phosphate is a precursor in formation of pathologic mineral deposit. This new insight into the mechanism of formation of mineral promises eventual control of pathological mineralization.

Medical Materials and Improved Surgical Bone Cement

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A biocompatible tissue adhesive bonding to bone would find many applications in orthopaedics. Oligomers or copolymers of 2-isocyanatoethyl methacrylate (IEM) or m-isopropenyl α,α-dimethylbenzyl isocyanate (TMI) have been synthesized. These low molecular weight liquids containing pendant isocyanate and ester groups were obtained on reacting IEM or TMI with ethyl acrylate, butyl methacrylate (BMA) or other acrylic monomers. Shear and tensile strength on bone treated with dil. aq. glutaraldehyde and then with either a solution of (1) IEM, (2) TMI, (3) IEM-TMI-BMA or (4) TMI-BMA bonded to polymerizable dimethacrylate was determined. The tensile adhesion of bone cemented with these compositions varied from 80 to 101 kg/cm^2 yielding stronger more permanent bonds than 2-cyanoacrylates or other adhesives previously suggested for the cementation to bone. On thermocycling for one week between 5° and 55°C H_2O, bond strength from 75 to 90 kg/cm^2 were obtained indicating that there is little deterioration of the bond on prolonged water exposure. Subject to their biocompatibility, compositions containing the oligomers of IEM or TMI should be most useful as adhesives for mineralized tissues.

Homogeneous, radiopaque bone cements incorporating 10% pentabromophenyl methacrylate have been formulated. Such materials had excellent physical properties, but the storage stability of their monomeric solution was inadequate. To overcome this, poly(methyl methacrylate-co-pentabromophenyl methacrylate) has been prepared. Evaluation of cured bone cements using this copolymer are under active investigation.

We have developed instrumentation to test experimental biodegradable bone plates in a project for the Army Institute of Dental Research. Results of the initial tests are that the bone plates degrade too rapidly. After one day of implantation, the original properties had degraded significantly and at the end of one week the plates had fragmented and were unsuitable for testing (hence, unsuitable as structural implants).

OUTPUTS/INTERACTIONS

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Technical and Professional Committees: Leadership Activities

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Alpha Chi Sigma
    G. M. Brauer, Member, Awards Committee

American Academy of Gold Foil Operators
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                        #43 - Dispersers for Alloy & Mercury
                        #55 - Electrically Powered Amalgamators

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Industrial and Academic Interactions

Industrial

Work with the Gas Research Institute is leading to reference and standard polyethylene resins, piping, and joints of the sort used in natural gas distribution systems. These materials will facilitate test method development, standardization of test methods, and inter-laboratory comparisons of test data. It is anticipated that the standard PE materials will be widely used by other sectors of the plastics industry.

A joint program is underway with Hercules, Hexcel, and NASA Langley Research Center to study delamination in composite materials. Hercules and Hexcel are providing materials and some fracture surface analysis, NASA is characterizing the samples, and NBS is determining the interlaminar fracture behavior. The objective is to establish the relationship between the properties of the composite and the behavior of its constituent materials.

Joint projects with Exxon, IBM, Eastman Kodak, and Armstrong World Inc. are concerned with polymer blends phase relationship and phase stabilization. Research activities are directed to specific polymer blends of interest to Exxon, IBM, and Eastman Kodak, to stabilization problems of concern to IBM and Eastman Kodak and to the barrier material property and processing of Armstrong World Inc. materials.

A joint project with scientists at the Almaden Research Laboratory of IBM and the CRM - Strasbourg, France led to the publication of the manuscript "The Molecular Weight Dependence of the Zero Shear Viscosity of Cyclic Polystyrene Molecules in the Melt".

Research Associate agreements have been concluded with Westinghouse Electric Corporation to transfer measurement techniques of compliant piezoelectrics, with IMASS Corporation to transfer design of time domain dielectric spectrometer for commercial development, and with General Electric Corporation to duplicate time domain dielectric spectrometer for use in its corporate research laboratories.

A joint research program has been established with Dr. T. T. Wang of the Bell Laboratories to develop a technique for real-time, in-situ fluorescence monitoring of the formation of polyimide polymers from poly(amide-acid) polymers.

The American dental industries continued to display strong interest in and support for the dental materials program. The research associate agreement with Dentsply International was extended to its third year and another dental manufacturer, Astron dental corporation, entered into a research associate agreement. One dental manufacturer supplied special alloy for porcelain fused-to-metal strength studies and other provided a new composite for NBS scientific research. Glass inserts for composite restorations have generated much commercial interest. NBS-developed monomer for radiopaque polymers was trial-synthesized by one dental supplier.

Work continued with scientists at the Pulp and Paper Institute utilizing NMR to characterize the solid state morphology of native cellulose. A paper has been written on this work.

Industrial/Academic

A cooperative program has been established to investigate the network structure of epoxy resins and other thermosets. Prof. R. Stein of the University of Massachusetts and H. G. Waddill of Texaco are participating in this effort. A postdoctoral Researcher from Prof. Stein's group has been assigned to work part time at NBS to collect and analyze neutron scattering data from epoxies swollen with deuterated solvent. Thermo-analysis of the epoxy samples to determine the glass transition temperature has been carried out at the University of Massachusetts. Texaco is providing the raw materials and other mechanical measurements. The molecular weight determination of the curing agents and the epoxy resins were also carried out at Texaco. The objective of this project is to understand the basic network structure in highly crosslinked polymers and to determine the relation among network structure, processing condition and physical properties.

An NBS/Mobil/Univ. of Massachusetts joint project is concerned with polystyrene/poly(p-methylstyrene) blends. Phase diagram and binary interaction parameter between different monomers are being measured by SANS technique at NBS. A second project is an NBS/GenCorp/Univ. of Kyoto joint effort on rubber/rubber blends. Questions of microstructure and isotope effects on the miscibility and phase diagram are being addressed. For immiscible rubber/rubber pairs, the mechanical blending/phase separation process will be studied. This information is critically needed by the tire industry.

Academic

A joint research program is underway with Prof. E.-S. Wu of the University of Maryland (Baltimore County) to measure, by fluorescence recovery after photobleaching, the self-diffusion of polymers in entangled system as well as the diffusion of small molecules in entangled polymer solutions and in plasticized polymers.

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

A joint research program to study the conformation of block copolymers in phase-separation systems has been established with Prof. J. Koberstein of University of Connecticut. As part of this program, a graduate student is conducting neutron scattering measurements on these polymers at NBS.

Work on the characterization of the mechanical response of cyclic polystyrenes, in conjunction with the University of Pittsburgh, led to the publication of two articles. NBS scientists furnished the sample and interpreted the data while scientists at the University of Pittsburgh developed mechanical testing equipment suitable for studies on very small amounts of material.

A collaborative effort has been initiated with the University of California, Santa Barbara to build a tunneling electron microscope in the Polymers Division at NBS. A first generation apparatus has been constructed and tested at NBS.

Collaborative programs with universities in the area of polymer blends include single chain conformational and diffusional studies in polymer blends and solutions with the Universities of Wisconsin and Minnesota. Also, we have an ongoing international collaboration program with Nagoya University, Japan which is jointly sponsored by NSF/JSPS on the subject of block copolymers in microphase-separation systems.

Guest scientists from six domestic and three foreign institutes are conducting research on dental materials at NBS. A cooperative seminar series was established with the University of Maryland Dental School. Several finite element modeling studies on dental material-tooth systems continue with the University of Illinois, Chicago. One guest scientist from Georgetown University is a key investigator on bonding of dental resins to dentin. Guest scientists (residents) from the Naval Dental School work with several investigators within the group. We acknowledge the cooperation of Professor E. Horowitz from John Hopkins University, Professors L. Queral and M. Sadovnik from the University of Maryland, and Dr. W. Pierce from Hershey Medical Center on studies of cardiovascular plaque.

Associated Activities

Invited Talks

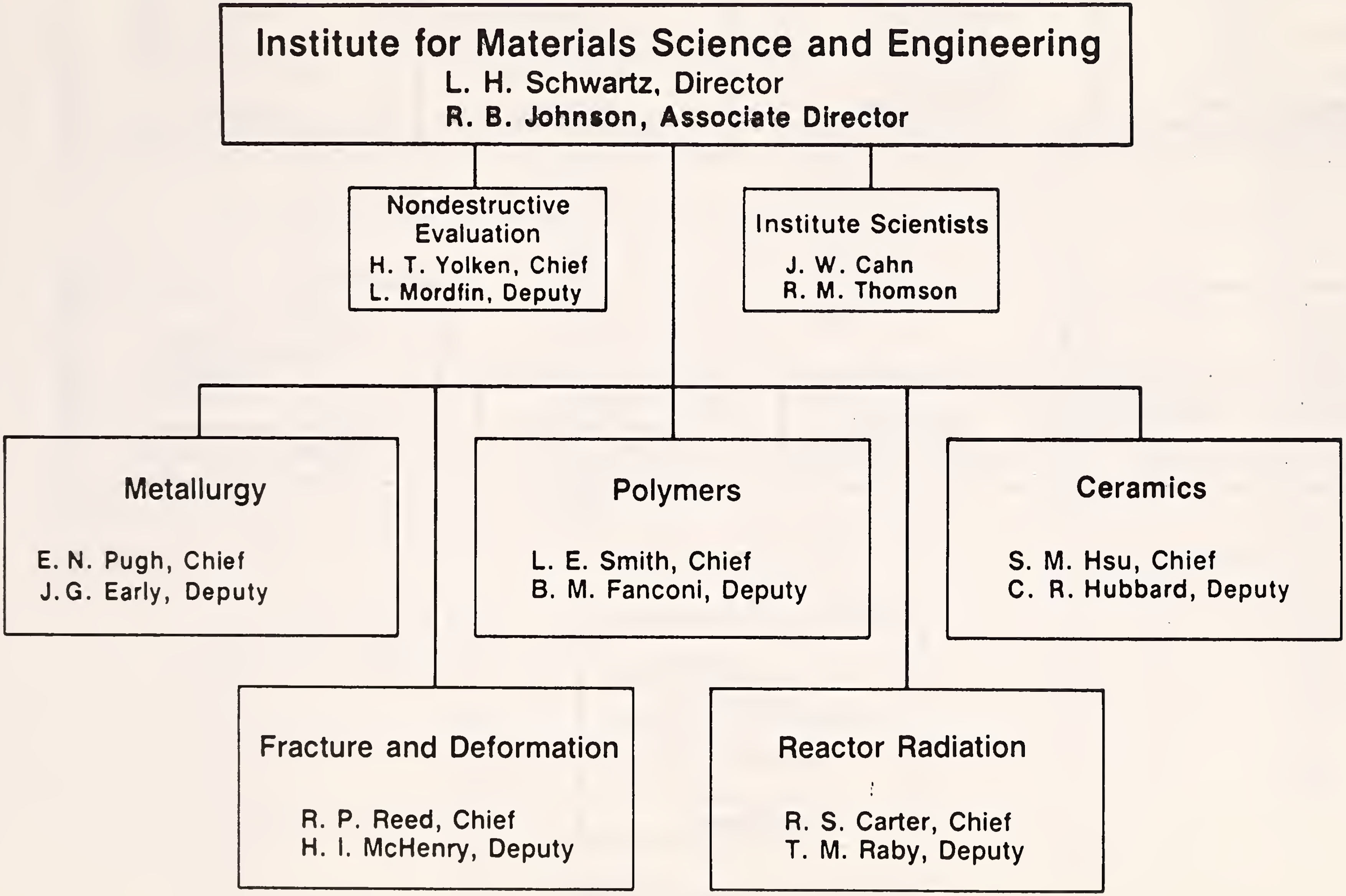
Division personnel presented a total of 108 invited talks on research activities at the following types of organizations and symposia: industrial laboratories,12; international symposia, 9; universities, 34; topical symposia 11; national and government laboratories, 15; professional society meetings, 18; and Gordon Conferences, 9.

SRMs

The certificate for one of the poly(methyl methacrylate) SRMs has been issued (SRM 1489) and the certificate for the other (SRM 1488) is being drafted. These SRMs will be used by the polymers industry to calibrate instruments used to measure the molecular weight and molecular weight distributions of acrylic type polymers.

Patents

G. T. Davis, C. K. Chiang, J. M. Antonucci, and T. Takahashi, Polyethylene Imine-Metal Salt Solid Electrolyte, US Patent No. 4,576,882, March 18. 1986.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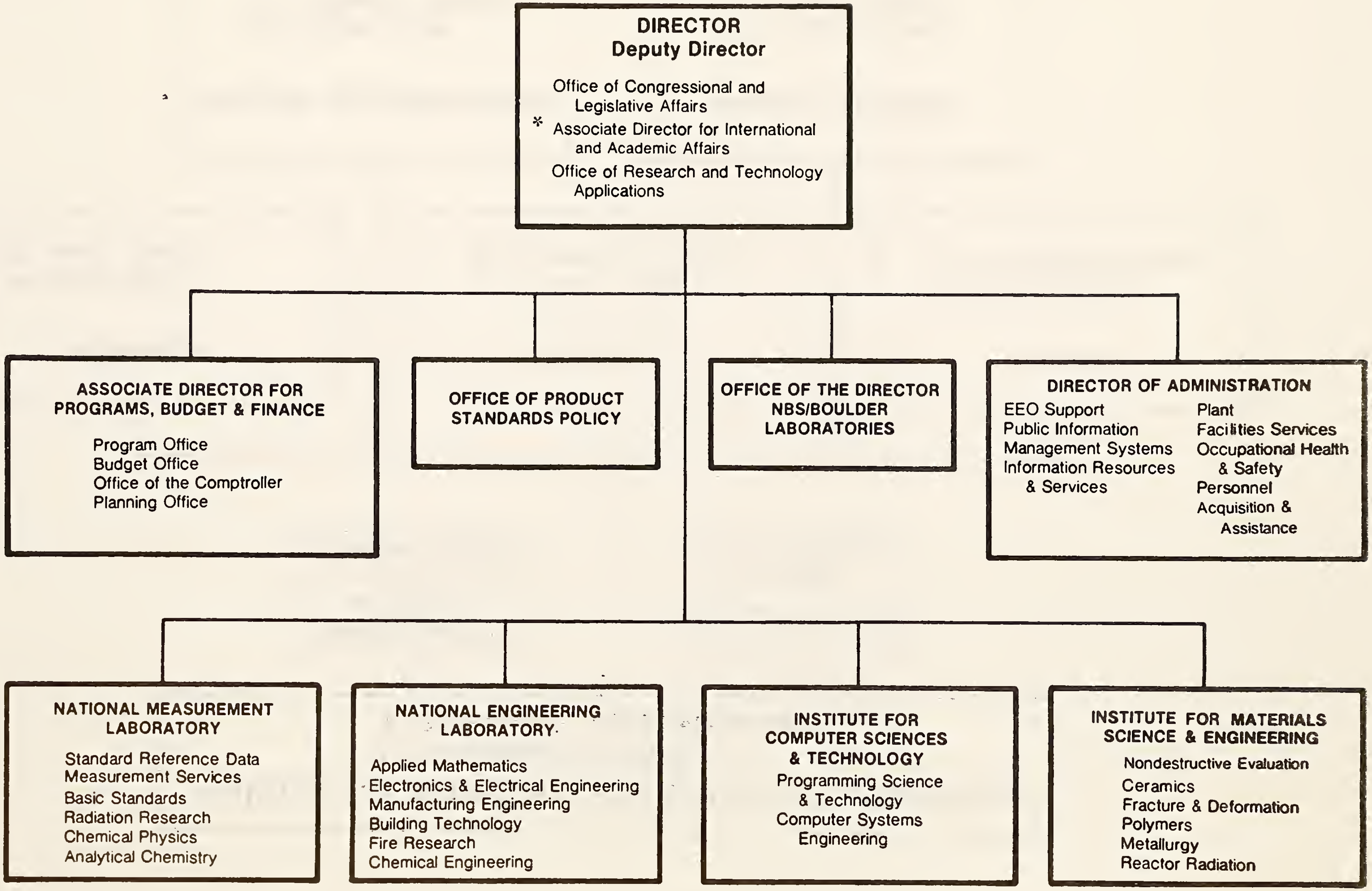

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10. SUPPLEMENTARY NOTES

☐ 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 86 are reviewed. Included are descriptions of the 6 Tasks of the Division, project reports, publications, and other technical activities.

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

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

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