Center for
Materials Science

Polymers Division

Technical Activities 1984

NBSIR 84-2946
January 1985

U.S. Department of Commerce
National Bureau of Standards

Center for
Materials Science

Polymers Division

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

Technical Activities 1984

NBSIR 84-2946
January 1985

U.S. Department of Commerce
National Bureau of Standards

TABLE OF CONTENTS

PAGE

POLYMERS DIVISION (440)

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

Since their commercial introduction in the early part of the twentieth century, synthetic polymers have rapidly grown to become indispensable materials in our technology-based economy. 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. Recent summaries show that industrial research on polymers and polymer composites accounts for nearly half of the total industrial R&D expenditures on metals, polymers, and inorganic materials.

Polymers have been shaped by intellectually sophisticated research which has been recognized by a number of Nobel Prizes. The resulting materials have contributed to national industrial productivity through their economy, ease of fabrication, and useful properties such as low density, corrosion resistance, and toughness. Polymers are energy efficient; the largest volume polymer, polyethylene, uses 29 percent of the energy per unit volume required by steel for conversion from raw to refined material and yields further savings in processing and shipping. In fact, studies have shown that for every barrel of oil used to make plastic products, approximately one barrel is saved in comparison with the use of the next best alternative material. These characteristics have enabled polymers to contribute to increased national economic strength both by creating entirely new products and by substituting for other materials in existing products.

Polymers have entered a widening range of increasing sophisticated and demanding applications. Polyvinylidene fluoride films are used as piezoelectric transducers, biomedical imaging devices and infrared sensors. Structural parts of aircraft are constructed from composites with a polymer matrix and sometimes a polymer reinforcement. Polyurethane elastomers are used to pump blood in circulatory assist devices. The list of such examples is very long, and includes trends for the increased use of polymers in packaging, construction, transportation, national security, electronics, information handling, clothing, electrical appliances, energy, dentistry, and medicine.

The Polymers Division is responsible for providing standards, measurements, and fundamental concepts of polymer science to assist U.S. industry and remove barriers to economic growth. Increasing usage and changing applications create many new needs for Division programs. To identify key needs with the highest prospects for payoff and to coordinate Division programs, with those of other laboratories, the managers of the Polymers Division make structured visits to industrial and Government laboratories. Visited sites include Bell Laboratories, E. I. DuPont de Nemours, Inc., 3M, Army R&D Command, General Motors Corporation, Martin

Marietta and Lawrence Livermore Laboratories. Surveys have been conducted in the areas of durability, composites, and processing. Research Associates, working on joint NBS-industrial projects in polymers were sponsored by ten organizations during the past year including General Electric Research Laboratories, Exxon Chemical Co., Bethlehem Steel, Arco Chemical Co., and the American Dental Association. These and other contacts with research associates, experts in industry, trade associations, standards associations, Government, and universities ensure that the Division's efforts are directed toward fostering the effective use of polymers in solving generic national problems. These include economic growth, international competitiveness, national security, and efficiency in Government.

Current activities are concerned with phase behavior and characterization methods for polymer blends, processing and reliability of composites, long-term research on the scientific basis for mechanical reliability in load-bearing applications, chemical durability, lifetime prediction, migration of protective additives, characterization methods, standards for molecular composition and performance properties, dielectric properties, and reliable dental and medical materials. Substantial cooperative efforts are conducted with research associates from a number of industries, universities, and other government agencies. All these efforts have led the staff of the Division to engage in highly productive research that is outlined in this report. Some of the more significant accomplishments of the last year are described below.

FY 84 SIGNIFICANT ACCOMPLISHMENTS

- POLYMER STANDARDS AND CHEMICAL PERFORMANCE
  TASK 15432

Three poly (methyl methacrylate) polymers to be used to produce narrow-molecular-weight-distribution Standard Reference Materials have been obtained. They have molecular weights of approximately 120,000, 30,000 and 10,000 with polydispersities of less than 1.2. A preliminary limiting viscosity number (intrinsic viscosity) of the highest molecular weight polymer in toluene has been measured in order to establish the proper experimental conditions for the actual runs which will determine the final certificate value for this quantity.

A critical evaluation of the Mark-Houwink parameters used in determination of the molecular weight of linear polyethylene has been completed. Values of these parameters for six solvents commonly used for viscosity and size exclusion chromatography measurements were critically evaluated for publication in the Journal of Physical and Chemical Reference Data. A similar critical evaluation has been carried out for atactic polystyrene in five frequently used solvents.

A polystyrene polymer of narrow molecular weight distribution has been fluorescently labeled with nitrobenzoxadiazole (NBD). The self-diffusion coefficient of this NBD-labeled polystyrene in polystyrene-diethyl phthalate solutions has been measured by the method of fluorescence recovery after photobleaching. For the NBD-labeled polystyrene with a molecular weight of 110,000, in the semi-dilute concentration region from 0.07 g/ml to 0.3 g/ml, the dependence of the self-diffusion coefficient on polymer concentration agrees with the predictions of scaling and reptation theories.

The hydrolytic stability of poly(ethylene terephthalate) has been studied in order to predict its long term behavior as the base for film and magnetic tape. It was found that the hydrolytic damage in poly(ethylene terephthalate) can be detected rapidly and non-destructively by infrared measurements long before physical deterioration becomes important.

The wavelength dependence of degradation in molecular weight in a common glazing material poly (methyl methacrylate) due to chain scission was shown to be linearly related to the energy of the radiation in the 300 to 360 nm range of the solar spectrum. Above 365 nm, there was no photolytic effect. The results show that the shorter UV wavelengths cause the most damage, and that the absorber is the polymer itself rather than some sensitizing impurity.

The major effect of water present as 95% relative humidity at elevated temperatures (70 to 90 °C) on the thermal degradation of commercial poly(methyl methacrylate) containing UV absorber was shown to be to replace some of the air in the ambient atmosphere and hence decrease the amount of oxidative degradation.

- BLENDS PROCESING
  TASK 15433

Small angle neutron scattering (SANS) has been used to obtain both cloud point and spinodal curves for a series of deuterated polystyrene (PS) and poly (vinyl methyl ether) (PVME) blends. The correlation length (ξ) associated with concentration fluctuations and the binary interaction parameter (χ) have been determined as a function of temperature and composition.

Several hundred grams of PVME, required for blend studies, have been synthesized by a cationic polymerization. Fractionated samples range in molecular weight from 10^5 to 1.5×10^6 with a polydispersity ratio as low as 1.3. Mark-Houwink parameters have been determined in MEK and THF.

Using scaling concepts, it has been shown that a universal coexistence curve can be constructed for binary polymer/solvent systems which is explicitly independent of molecular weight. A major complexity of polymer phase diagrams is that they depend on the molecular weights of the constituent polymers in addition to the usual concentration and temperature variables. This universal phase diagram provides a useful interpolation and extrapolation scheme for polymer/solvent phase diagrams.

SANS experiments have been performed on a series of polyether/polyurethane block copolymers. The soft polyether block was deuterolabelled. The scattering data yield a radius of gyration for the polyether chains that is substantially larger than that for the unperturbed dimensions. This implies that the chains are in extended conformations consistent with recently developed theory.

A statistical theory of block copolymers in a lamellar morphology suggests that the chain are stretched out (oriented perpendicular to the lamellar surfaces). Qualitatively, this effect arises from a balance between interfacial and elastic forces. Domain thicknesses are predicted to vary as the 2/3 power of the chain length.

Small Angle X-ray Scattering Facility: Initial site preparation is essentially complete with installation of the x-ray generator expected to be completed by the end of FY 84. Data acquisition and control computer and the color graphics display system have been acquired and installed. Facility is expected to be operational in early 1985.

- TESTS, STANDARDS AND CHARACTERIZATION FOR MANUFACTURING AND DURABILITY OF DENTAL AND MEDICAL MATERIALS
  TASK 15435

A castability value, C_v, for several dental alloys was determined as the percentage of cast segments of a polyester grid pattern. C_v was evaluated as a function of alloy and mold temperature. Chemical analysis was used to determine the elemental composition of each alloy. The resultant equations are useful for design of new alloys in the Ni-Cr system.

The National Institute of Dental Research and the National Bureau of Standards entered into a joint agreement for working on the chemistry of calcium phosphate compounds as related to living systems.

The Research Associate agreement between Dentsply International and NBS was effected for studying the basic chemistry and structure of hydrophobic dental composites.

Temperature dependent elastic properties of two dental porcelains and three alloys were determined. These are useful for analysis of thermomechanical stress as developed in porcelain-alloy systems.

Clinical studies of the wear of dental composites revealed that no simple relationship exists between curing method, filler content, resin bases and wear resistance.

Multivariant analysis of the results of solubility studies of dental porcelains with differing compositions has been completed. The resulting equation may be used as an aid in designing new porcelains with specific properties and acceptable resistance to degradation by oral fluids and foods.

Adhesion to tooth studies showed that NPG (N-phenyl glycine) can be substituted for NPG-GMA (the addition adduct of N-phenyl glycine and glycidal methacrylate) without substantial change in the bond strengths. NPG is expected to be more stable.

A scheme of measuring the oral environmental resistance of composites to degradation was developed. The resistance index, R, is designated to represent the softening resistance of the matrix resins under the influence of various ingredients within the oral environment. Twelve commercial composites have been evaluated using this method, so far the comparison between the R rating and the clinical performance of three composites reported in the literature is rather encouraging.

A dilatometer for measuring the polymerization shrinkage of polymers was designed and fabricated. Shrinkage during polymerization is particularly important as it relates to both durability and marginal leakage of dental compositesr restorations.

Improved topical fluoridation procedures: On the basis of fundamental studies, it was concluded that presently used topical fluoride treatments are limited in their effectiveness due to one or more of the following: (1) the bulk of the fluoride deposited by the treatment is in a form that is unstable in the mouth, (2) the small amount of permanently-bound fluoride does not penetrate into the enamel crystals, and (3) the treatment does not deposit sufficient fluoride into those areas of the tooth that need the caries protection most, i.e. the interproximal areas and pits and fissures. A new procedure was developed which would significantly reduce all of these limitations. Laboratory, animal, and limited clinical studies have all shown that treatments based on this procedure incorporate more permanently-bound fluoride into enamel than those in clinical use. However, it remains to be shown that they are superior in preventing cavities. The new treatment has a number of modalities, and additional research is needed to choose the ones that are most suitable. The procedure also has the potential to remineralize as it fluoridates the enamel in white spots. It is likely that this research will lead to new types of procedures in dental practice.

Calcium phosphate setting cements and demineralizing slurries: The work conducted previously in our laboratories has led to the discovery that certain combinations of calcium phosphates, when mixed with water to form paste, will harden into a mass which has the same composition as tooth and bone mineral. This cement is especially compatible with soft tissues and is a candidate for a large number of dental and medical applications (as materials for pulp capping endodontic treatments, bone replacement, alveolar ridge augmentation, periodontal therapy, etc.) When applied as a slurry, the mixture has possible use as a remineralizer for incipient carious lesions, as a desensitizer for exposed roots, and as a remineralizing tooth paste. In collaboration with the American Dental Association Health Foundation's Research Institute, a study to test the biocompatibility of the cement using animal models has been completed. The results show the calcium phosphate cement to be neither toxic nor mutagenic. Preformed implants, made from the cement mixture, were well tolerated by the animals and caused no adverse tissue reactions. These results encourage further functional evaluation of the material for a number of these applications.

Improvement in vanillate cements: The properties of the vanillate cements previously developed in this laboratory were further improved by incorporating propionic acid coated zinc oxide as a minor constituent of the powder. Cements with shorter setting time, film thicknesses as low as 7 µm and decreased brittleness were obtained. Adhesion of these materials after 24 hours water exposure is excellent and better than that of ionomer cements. Thus, mean bond strength to stainless steel is 18.3 MPa. Incorporation of sodium fluoride into vanillate and syringate cements yields materials with adequate setting time and strength and which release fluoride for weeks. Such materials may reduce caries formation in areas adjacent to them.
A new monomer: 3,3-dimethyl-9-methylene-1,5,7,11-tetraoxaspiro [5.5] undecane (I), has been synthesized. This free radical cured monomer which expands on polymerization may have a wide range of applications due to its low melting point of 32 °C . This compound was prepared to develop a procedure for synthesizing substituted, unsymmetrical spiro ortho-carbonate monomers. A method has been developed to yield highly substituted, novel thiocarbonate intermediates which will lead directly to the target monomer compounds.

The feasibility of preparing extremely hydrophobic, mechanically strong esthetic dental composites from a series of highly fluorinated resin systems was demonstrated: A new, versatile class of dental cements based on dimer and trimer acids was developed. Many of these cements have energy-absorbing qualities and a high degree of water repellancy. Some of these cement formulations exhibit the remarkable property of expanding rather than contracting on setting. A non-discoloring, chemical initiator system was developed for the ambient polymerization of resin based dental materials based on the use of polythiols and organic hydroperoxides.

Improvement in Bone Cement: Evaluation of compositions incorporating a novel inhibitor, accelerator and chain transfer agent, to make them more biocompatible and to reduce their peak temperature obtained on polymerization, surpassed, often by a wide margin, all requirements of the specification for bone cements. Physical properties are also upgraded by replacing the $BaSO_4$ radiopacifying filler with a highly brominated monomer such as pentabromophenyl methacrylate which with methyl methacrylate yields a homogeneous copolymer having a high degree of radiopacity. An effort is being made to synthesize suitable iodine containing methacrylates as radiopacifying agents for medical implants. Potential use of vanillate cements as coupling agents for metallic implants has been explored and looks promising because of their strong bonding to chrome-cobalt alloys and acrylic composites.

- MECHANICAL PERFORMANCE OF POLYMERS
TASK 15436

The role of carbon bond scission in the mechanical degradation of polystyrene has been elucidated by investigations of free radical generation, molecular weight degradation by viscometry, and molecular end group formation by Fourier transform infrared spectroscopy (FTIR). It was concluded that free radical propagation reactions are negligible in this glassy polymer compared to the case of semicrystalline polyethylene. A study of bond scission as a function of molecular weight revealed no significant trend when mechanical degradation is carried out at cryogenic temperatures.

An examination of PET fibers of the sort used in tires has revealed the nature of microstructural changes occurring during thermal treatment. It was found by solid state NMR that the relative change in surface area between the crystalline and noncrystalline regions was 10% for annealing at 200 °C and 30% for annealing at 257 °C relative to the unannealed fiber. In addition, it was established that the crystalline thickness changed from about 3.5 nm to 7 nm when the fibers were annealed.

The structure and mechanical properties of polyethylene films used in helium filled, heavy lift balloons for atmospheric research has been investigated to determine possible causes of recent failures experienced in the launch of these balloons by NASA. Molecular weight distributions, methyl group contents, melting characteristics, orientation of the crystalline regions, densities, and extensions-to-break at 23 and -70 °C were determined for a number of films. Differences were found in molecular weight distributions and mechanical properties. Additional investigations are underway to determine whether these differences are significant in terms of balloon performance.

A materials handbook containing information on the two principal polymeric materials used in orthopedic devices has been prepared for the Food and Drug Administration. Included in the handbook are specifications, raw materials characterization, processing information, mechanical properties, wear characteristics, and effects of high energy radiation. The report is intended for distribution to the FDA, resin manufacturers, fabricators, medical researchers, and surgeons.

Investigations of the long time creep and recovery behavior of ultrahigh molecular weight polyethylene and its dependence on temperature have shown that existing models of creep are inadequate. At times under creep greater than 10^5 s an abrupt break occurs in the creep curve which is not predicted by existing models. Additional experiments are underway to obtain a more complete description of the dependence of both the recoverable and nonrecoverable components of creep on time and temperature.

- PROCESSING AND RELIABILITY OF POLYMER COMPOSITES
  TASK 15437

A major concern in polymer composites is their susceptibility to the initiation and growth of damage in the matrix resin between the fibers. One potential approach to this problem is the use of high toughness polymers. A systematic study was conducted using 21 different composite system. A clear correlation was developed between the fracture energy of the polymer resin and the interlaminar fracture energy of the composite. This provides fundamental data necessary to scientifically design composites. Composites made with thermoplastic resins have generated a great deal of interest lately because they are thought to be very resistant to the initiation and growth of interlaminar damage. Four different thermoplastic composites have been tested, and it was found that their interlaminar fracture energies were actually less than those obtained for thermoset composites where the thermoset resin had the same fracture energy as the thermoplastic resin. Examination of the fracture surfaces for the composite specimens revealed considerable interfacial failure associated with the thermoplastic. This suggests that poor fiber-matrix bonding can significantly limit the delamination resistance of thermoplastic composites.

Small angle neutron scattering (SANS) has been applied successfully to quantify the delamination process in fiber reinforced composites. The background scattering problem encountered in x-ray technique can be circumvented in the present case by matching the scattering length of the fibers and the matrix resins. Average size of the microcrack and the total crack surface area can be determined with the SANS technique.

Both theoretical and experimental neutron scattering studies have been carried out to elucidate the molecular network of epoxies. Certain portions of the epoxies network were selectively labelled with deuterium, and the neutron scattering data from these labelled specimens were collected. Both the first and the second moments of the correlation distance distribution of the crosslinks has been determined.

The failure behavior of rubber-modified epoxies is of great importance because these very tough materials are widely used in adhesives and composites. Their complex and highly viscoelastic fracture properties were studied extensively, and a failure prediction criterion was developed based on a simple crack blunting model. This criterion says that fracture occurs only when a critical stress level is reached at a critical distance ahead of the crack tip. This criterion successfully predicts fracture over a wide range of test conditions and may provide new insights into the molecular mechanisms of failure for these materials.

- MICROSTRUCTURE AND PERFORMANCE OF DIELECTRIC PLASTICS
  TASK 15439

The evolution of dielectric properties during the curing of epoxy resins has been measured by a time-domain dielectric spectrometer. Since these properties at the early stages of cure are dominated by conductivity, an automated measurement system for AC conductivity has been designed and built.

Work has begun on developing a stable material which will duplicate the dielectric and thermal properties of living tissues to be used in the calibrating and testing of devices which subject portions of the human body to high frequency electromagnetic radiation. A theoretical study of the diffusion of interacting charged particles in an applied field is aimed at understanding the relative role of space charge and interfacial polarization in the dielectric properties of the system.

Linear polyethyleneimine has been synthesized and its ability to dissolve salts and conduct ions has been demonstrated. As sodium iodide concentration in the polymer is increased, polymer crystallinity is at first decreased but then increased as a high-melting crystalline complex is formed involving the polymer and salt. Such behavior is analogous to that of polyethylene oxide.

A Research Associate agreement between NBS and the Homer Research Laboratories of Bethlehem Steel Corporation has been reached. The work will focus on transferring our technology for producing piezoelectric polymers to oriented polymers resulting from a unique biaxial hydrostatic extrusion process employed at Bethlehem Steel.

A pressure gauge based on piezoelectric polyvinylidenefluoride which compensates for adiabatic heating of the surroundings has been developed and successfully field tested in a project sponsored by the Air Force.

POLYMER STANDARDS AND CHEMICAL PERFORMANCE
Task 15432

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

Polymeric SRMs certified for molecular weight are needed by the polymer industry to calibrate gel permeation chromatographs (GPCs), the most widely used instruments for polymer characterization. In collaboration with the Department of the Navy, we began this year the characterization of three poly(methyl methacrylate) polymers which will be issued as SRMs.

Improved techniques for polymer characterization and better understanding of polymer solution properties are essential to the efficient production of polymeric SRMs. 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."

Research this year on degradation mechanisms and rates includes investigations of the hydrolysis of polyester-based recording media, the hydrolysis of cross-linked polyurethanes, and the degradation of polyurethane tubing in media simulating body fluids. In addition, we have carried out a collaborative program with the Building Materials Division to investigate the kinetics and mechanism of the photolytic and thermal degradation of poly(methyl methacrylate), a widely used material for solar cover plates.

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. Work this year on the migration of additives includes measurements of diffusion rates by the solvent extraction method and by the concentration profile method, and investigations of polymer self-diffusion in concentrated solution by the method of fluorescence recovery after photobleaching.

Critical Evaluation of Mark-Houwink Relation for Linear Polyethylene

Subtask 1 of Task 15432

H. L. Wagner

One of the most important physical properties of a polymer is its average molecular weight, which largely determines its processibility and its 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 (GPC), are used instead..

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

$$\mathrm{LVN} = [\eta] = KM^{a}$$

where K and a are empirical constants 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 uncertainty. Determinations such as these were rejected in favor of direct determinations of molecular weight by absolute methods such as light scattering or osmotic pressure.

The literature for linear polyethylene has been critically reviewed and the K and a values for six solvents, commonly used for viscosity and size exclusion chromatography, have been recommended. These solvents are decalin, 1,2,4-trichlorobenzene, 1-chloronapthalene, tetralin, o-dichlorobenzene and p-xylene. In addition the literature values of K for several different theta solvents ($a = 0.5$) are presented.

A review paper has been written and submitted to the Journal of Physical and Chemical Reference Data.

A similar critical evaluation has been undertaken for atactic polystyrene. The viscosity-molecular weight data for five frequently used solvents are being reviewed. These are benzene, butanone, chloroform, toluene, o-dichlorobenzene and 1,2,4 trichlorobenzene. Two important theta solvents will be included in the review, namely cyclohexane and decalin.

Poly (methyl methacrylate) Standard Reference Material
Subtask 2 of Task 15432

H. L. Wagner

A sample of poly (methyl-methacrylate) of about 120,000 molecular weight and a weight to number average molecular weight of 1.07, proposed for use as a Standard Reference Material, has been blended and examined for homogeneity by viscosity. Measurements of six different parts of the sample, chosen randomly, revealed no difference in limiting viscosity number (intrinsic viscosity) within sample measurement error. Thus there is no evidence of sample heterogeneity.

To determine volatile content, some of the material was pumped at 60 °C through a liquid nitrogen trap at a pressure of about 10^{-4} mm on a high vacuum line. After about a day a weight loss of 0.7% occurred, which was regained on exposure to air. The same weight loss occurred in a dessicator, indicating this change is probably due to moisture. The material should therefore be stored in a dessicator before being weighed.

Preliminary viscosity determinations were made to establish the range of concentrations in which the viscosity number is linear with concentration. This is needed to establish the maximum concentration for the measurement of limiting viscosity number for the SRM certificate. Since there was no sign of curvature up to at least 0.01 g/ml, there should be no problem with linearity if the concentrations are kept below this value.

Rubber and Rubber Compounding Standard Reference Materials
Subtask 3 of Task 15432

G. W. Bullman and G. B. McKenna

NBS provides rubber and rubber compounding Standard Reference Materials that are used by the rubber industry for quality control in production of rubber and its processing into articles. During the past year, recertification of SRM 384 (N-t-butyl-benzothiazole-sulfenamide) has been completed. This compounding material is in ASTM Standards as a reference ingredient in standard rubber compounds.

Self-Calibrating Gel Permeation Chromatography
Subtask 4 of Task 15432

P. H. Verdier

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.

During the current year, construction of a new scattering cell of improved design was completed. Tests of the new cell showed it to have much less stray light than had been observed with its predecessor, but still too much to enable high-quality measurements to be made. Current efforts are directed at further improvements in cell design and at modification of the optics to improve the optical quality of the incident beam.

Fluorescence Spectroscopy of Rigid Rod-like Polymers

Subtask 5 of Task 15432

W. H. Grant, R. E. Lowry, B. F. Howell, F. W. Wang, and C. M. Guttman

Recently, heterocyclic rigid-rod polymers, exhibiting properties such as high tensile strength, high modulus and thermal and oxidative resistance 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 the 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 solution for 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.

Preliminary work on this project has just begun. The excitation and emission spectra of various films and formulations of rod-like polymers, such as poly(p-phenylene benzbisthiazole) (PBT), provided by AFWAL have been taken confirming that the polymers do indeed fluoresce. Furthermore, we have looked at the absorption and fluorescence spectra of soluble extracts obtained from some PBT films.

Automated Liquid Size Exclusion Chromatography
Subtask 6 of Task 15432

B. Dickens, F. L. McCrackin, and J. D. Barnes

Since vendors of chromatographic machinery generally treat their software as proprietary, it is difficult to evaluate the sources of variability in the analytical results. The NBS system for automated liquid size exclusion chromatography is intended to serve as a benchmark for improved standardization of analytical techniques in this area as well as an analytical instrument for use by NBS researchers in characterizing polymers encountered in their research.

We have improved our automated system for liquid size exclusion chromatography by including an option which estimates baselines and calculates molecular weights without requiring operator input. This procedure will soon be implemented in the online data collection system so that results will be available to the user immediately following an analysis.

Improved procedures for evaluating interpolating functions for column calibrations and for performing data reduction in batch mode have been implemented. Thus, the results are now more accurate and are more easily obtained.

The computer used to automate the chromatograph does not allow the user to process previously collected data at the same time that it is collecting new data. Therefore, efficient procedures are needed to allow the user to interactively examine and process chromatograms and molecular weight distributions. The data reduction programs will be modified to run on the VAX computer used to analyze small-angle x-ray scattering data. This machine allows multiple simultaneous users, has excellent interactive graphics, and provides much more mass storage than is available on the minicomputer used with the chromatograph. Database management tools will also be implemented on the VAX to permit ready tabulation of the results of chromatographic analyses and extraction of statistical correlations from them.

To obviate the necessity to guess satisfactory operating parameters prior to an analysis, we are currently studying ways to transmit control information from the minicomputer to the chromatograph during a chromatographic run or after a run has been completed to provide a rerun with a better choice of operating parameters. This would significantly increase the throughput of the instrument.

Joint work with J. Brown of the Center for Fire Research and H. L. Wagner of the Polymers Division has shown that degradation of standards representing polymer molecular weights is a problem when the solvent is unstable to oxidation and the standard contains tertiary carbon atoms. Thus, polystyrene in tetrahydrofuran is a particularly unstable combination which undergoes appreciable change in number average molecular weight over a few days when in contact with air. Conversely, polymers such as poly(methyl methacrylate), which does not contain tertiary carbon atoms, are effectively stable in tetrahydrofuran even when exposed to the atmosphere.

Molecular Weight Distribution of Ultra High Molecular Weight Polyethylene

Subtask 7 of Task 15432

H. L. Wagner

The clinically and industrially relevant properties of ultra high molecular weight polyethylene (UHMWPE) depend in large part on its exceptionally high molecular weight and molecular weight distribution. However, the ordinary techniques for measuring these and related quantities are subject to unusual problems. Because of the dependence of viscosity on shear rate, for example, limiting viscosity number cannot be readily determined in a capillary viscometer. A low shear rotational viscometer operating at high temperatures has been developed in this laboratory for this purpose.

Molecular weight distribution may ordinarily be determined by either fractionation or liquid size exclusion chromatography (GPC). A fractionation of a sample of UHMWPE was carried out by a hydrodynamically induced crystallization technique and the limiting viscosity number of each of 11 fractions was measured in the low shear rotational viscometer in decalin at 135 °C. Assuming that the Mark-Houwink relation, established for molecular weights up to about 1 million, holds for higher molecular weights, the molecular weights of the fractions calculated from this relation ranged from about 800,000 to 11 million. Despite the uncertainty in the absolute values, the general features of the integral molecular weight distribution curve are of interest. The molecular weight of the bulk of the material lies between 900,000 and 10 million and there is a suggestion of a bimodal distribution peaking at 1.1 million and 4.5 million. More than half the sample has a molecular weight of less than 2 million. Calculation of the weight average molecular weight from the fractions gave a value of 2.4 million and a number average molecular weight of 1.3 million.

The same material was separated by size exclusion chromatography using a newly developed type of column. Previous attempts using other columns resulted in clogging of the columns or in exclusion of the very high molecular weights from fractionation. There is some uncertainty in the calibration of this new column because calibrants above 20 million are unavailable. However, this would not account for the low value of 1.3 million for the weight average molecular weight of the same sample which gave a value of 2.4 million by ordinary fractionation. It is possible that at the high shear rate and temperature of the column some degradation occurred, or that some of the very high molecular weight species were filtered out by the apparatus. Hence, size exclusion chromatography using a commercial column is not a satisfactory method at this time for determining the molecular weight distribution of UHMWPE.

Translational Diffusion Constants of Linear and Branched Chains
Subtask 8 of Task 15432

C. M. Guttman

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 offers the hope of obtaining structural information about branching here-to-fore unavailable. Since the character and details of the branching of a polymer molecule determine its processibility as well as its ultimate physical properties and mechanical strength such information on branching is invaluable.

One theory currently available to relate these two quantities to the polymer structure 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 constant of a polymer molecule both branched and unbranched 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. Previously dynamic corrections to Kirkwood-Riseman theory were invoked to explain these descrepancies. Currently, work on branched chains is in progress.

In a second approach analytical modeling was done of 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 to the large M values used to compare with experiments were not possible even for polymers of high molecular weight. In this effort analytical modeling of chains with local structure and stiffness was done and the first two corrections to the large M limit of the hydrodynamic radius of the chains were computed exactly. It was shown the effect of chain structure on each of these three terms was different. Thus, the simple ideas of statistical length used earlier was found to need improving. This work has now been published.

In another approach Monte Carlo chains have been created in which corrections only up to the second cluster integral or the second virial are included in the modeling. Current work is going on showing that such chains at the theta point are akin to the so called "true" self avoiding walks. In the future, we plan to look into the importance of the third and higher cluster terms on size related properties, like hydrodynamic radius, for both linear and branched chains.

Dynamics of Polymer Chains
Subtask 9 of Task 15432

P. H. Verdier and D. E. Kranbuehl (William & Mary)

The dynamic behavior of polymer chains is important to improving both characterization and processibility of polymers. The principal methods used to estimate molecular weight, and in particular gel permeation chromatography, the only method available at present for estimating distribution in molecular weight, are dynamical, nonequilibrium experiments which depend in part upon the relaxation of polymer chains in dilute solution. 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 chain entanglements in a realistic way. Present work is aimed primarily at the study of entanglement 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.

Current efforts in this area are directed along two lines. The first is a series of studies to assess the magnitudes of artifacts in the results arising from the simplifications introduced in the simulation models (lattice constraints, local bead movement rules, etc.). The second is an attempt to make direct comparison of the results of our earlier simulation studies of concentrated solutions and melts with experimental results obtained elsewhere on concentrated solutions of polystyrene.

Monte Carlo Modeling of Chain Conformation in the Semicrystalline State of Polystyrene

Subtask 10 of Task 15432

C. M. Guttman, Z. Kifle[1], and J. D. Hoffman[1]

[1] Guest Workers, University of Maryland

The character of the chain trajectory in the semicrystalline state of polymer has been a matter of discussion for many years. The recent application of Small Angle Neutron Scattering (SANS) to such polymer systems allows a more direct measure of such chain trajectories. In recent years, a number of polymers in the semicrystalline state have been studied this way experimentally. However, most of the systems which have been studied have the problem that the deuterated chains often segregate from the protonated chains except under very rapid crystallization conditions. Thus, only rapidly crystallized polymer can be studied.

Polystyrene is one of the few polymers in which the deuterated chains and protonated chains show no signs of segregation under a variety of thermal treatments in the semicrystalline state. Taking advantage of this fact, Guenet has made a comprehensive experimental study of the SANS of isotatic polystyrene in a semicrystalline matrix.

In this work we are developing Monte Carlo models of chain trajectories of isotactic polystyrene in the semicrystalline state with the purpose of fitting Guenet's SANS data. The modeling is similar to that which we previously performed on polyethylene. Studies of models of folding on a variety of available crystal planes will be developed. The effects of thermal treatment on chain trajectory will also be studied.

Prediction of the Long Term Stability of Polyester-Based Recording Media

Subtask 11 of Task 15432

D. W. Brown

The stability of poly(ethylene terephthalate) is being studied over a five-year period for the National Archives in order to predict its long term behavior as the base for film and magnetic tape. Acid contents and mechanical properties of several types of film have been measured at intervals. Most film bases show barely significant changes in tensile strength and elongation after three years aging at 55 °C and 100% relative humidity, RH. However, two materials that had previously failed earlier than the others when aged at 85 °C have lost 30% and 95% of their initial elongation at break. Thus failure of these short-lived materials could be used to anticipate failure of the more stable materials. Films aged at 55 °C and 50% RH and those aged at 35 °C and 100% RH have not changed significantly.

A doubling of the initial acid content was previously taken as a safe limit for most of the films currently being aged. A good correlation has now been developed between increased acid content and increased absorbance at 3542 cm^{-1} and 3256 cm^{-1}. Absorption in these regions is attributed to

OH stretching in alcohol and acid, respectively. Changes in acid content can be measured rapidly and non-destructively with ample sensitivity to anticipate failure but it is necessary to remove any coating from a small portion of the film.

Aging of six brands of magnetic tape has continued. Measurements made include the force required to remove the oxide layer and the fraction of the binder soluble in tetrahydrofuran. Attempts are also being made to write and read information to and from aged tapes. The force required to remove the oxide layer can decrease very much from its initial value before the tape becomes unuseable. One curiosity is that the soluble fraction of binder goes through a maximum in tapes aged at 85 and 60 °C at 100% RH.

Hydrolytic Degradation of Cross-Linked Polyester Polyurethanes

Subtask 12 of Task 15432

D. W. Brown, R. E. Lowry, and L. E. Smith

The binder of magnetic tapes is a polyester polyurethane that has been cross-linked by chemical reaction with polyisocyanate. The presence of iron oxide makes the binder difficult to study. Model binder was prepared by cross-linking the urethane with known amounts of toluene diisocyanate. Hydrolysis was studied by various methods. Infrared measurements indicate that the acid content of the cross-linked model increases less rapidly on hydrolysis than in the parent polyester polyurethane. It was also found that the nitrogen content of highly aged samples was significantly more than that of the initial materials. We believe that polyester polyurethane that has been severely aged at high temperature and humidity loses polyester to the aging medium through evaporation. This probably accounts for the sol fraction of aged tapes going through a maximum with time.

Studies With Polyether Polyurethane Tubing

Subtask 13 of Task 15432

D. W. Brown, R. E. Lowry, and L. E. Smith

Polyether polyurethane tubing is used for electrical insulation on pacemaker leads implanted in blood vessels. Failures of this tubing have been reported but their causes and nature are in dispute. Stress cracking and enzymatic attack were put forward as causes of the failures. The Bureau of Medical Devices sponsored an in vitro aging study of tubing to help them assess the problem.

Tubing stretched on glass rods and aged in several media decreased in molecular weight. Something from the glass apparently attacked the polymer because much smaller effects were found in tubing stretched on Teflon rods. Bacteria were found in some media and it was possible that they had caused the degradation on Teflon. To resolve this question tubing was stretched uniaxially and biaxially on Teflon rods and aged in water and Ringers solution, with and without sodium azide, which acts as a bacteriocide. Samples were also aged in 0.3% hydrogen peroxide. Only these last degraded and that only by a small amount, compared with what had been found previously when hydrogen peroxide and had been used with lipids. No specimens failed mechanically. Thus our results do not support simple stress cracking as a cause of the failures found in use.

Factors in the Photolytic and Thermal Degradation of Poly(methylmethacrylate

Subtask 14 of Task 15432

B. Dickens, J. Martin[1], and D. Waxsman[1]

[1] Building Materials Division

The destructive effect of the environment on a transparent glazing material is being quantified in a joint program between the Polymers Division of the Center for Materials Science and the Building Materials Division of the Center for Building Technology. A chemical mechanism has been proposed to explain the deleterious effects of oxygen, unpolymerized raw material, and elevated temperature on poly(methyl methacrylate) (PMMA) exposed to solar-type radiation. The degradation causes scissions in the polymer chains, which gradually become too short to be able to confer the required mechanical properties on the glazing material. Thus, molecular weight changes as followed by gel permeation chromatography show the extent of damage.

Reprecipitated PMMA films were used to show that the wavelength dependence of the molecular scission process per absorbed photon for wavelengths in the solar spectrum lies in the following ratios: 1 (313 nm): 0.6 (335 nm): ~0.03 (365 nm): ~0 (405 nm). This shows that the short wavelength UV radiation is the most damaging part of the solar radiation. For degradation by 313 nm radiation, ready availabilty of oxygen was shown to increase the rate of scission (in thin films) by a factor of ~30 over the rate observed in the absence of oxygen.

Molecular weight profiles through the depth of the specimens have been used to study the interplay of oxygen diffusion and consumption rates in PMMA irradiated at various temperatures. The results reinforce our earlier conclusion that initiation of the damage process is caused by photolysis of the ester group in PMMA, and that the effect of temperature is mainly to increase the likelihood that the radicals produced from the ester group will diffuse apart before they can interact with one another. When the radicals diffuse apart, they cannot undergo self-anihilation by disproportionation. This allows other reactions, such as chain scission, to take place.

The effect of 95% RH at 70 and 90 °C on the long term thermal degradation of commercial PMMA containing UV-absorbers was examined. Water in the atmosphere in such quantities was shown to retard the degradation of the PMMA. Depth-profile analyses of the molecular weight in the specimens showed no dependence on sample thickness, as expected for these low rates of degradation. The mechanism is primarily one of oxygen depletion because such humid atmospheres contain 30% and 70%, respectively, of water vapor. The amount of oxygen dissolved in the specimen is significantly less in a PMMA specimen surrounded by very humid air at these temperatures than it is in a PMMA specimen surrounded by dry air at the same temperature.

Whether or not a radical interacts with oxygen depends on the local oxygen concentration in the bulk of the specimen, which in the presence of appreciable quantities of water vapor will be lower than in dry air. Since radicals give significantly more chain scission when oxygenated, a lack of oxygen corresponds to less chain scissions.

At 70 °C, the number of chain scissions increases linearly with time. At 90 °C, the number of chain scissions is proportional to the square root of time, but the constancy of the molecular weight profile with depth in the sample shows that even in this case the interior is not starved of oxygen because of the low rate of initiation. Relaxation of the matrix begins between 70 °C and 90 °C, and it is probable that its effect, the migration of free volume throughout the specimen and the separation by diffusion of free radicals which would otherwise anihilate one another, has the same square root of time dependence found for the bleaching of photochromic materials in glassy matrices by Kryszewski, Nadolski, North and Pethrick (J. Chem. Soc., Faraday II, 76, 351 1980). In our other work on the effect of water on PMMA degradation, water added in sealed cells to an already present dry air atmosphere did not change the amount of degradation significantly at 85 °C. Therefore, plasticization of the matrix by water is not significant at these temperatures where the matrix has already been plasticized somewhat by the temperature. Further work will examine the plasticizing effect of water at lower temperatures.

Photodimers in Polymer Matrices

Subtask 15 of Task 15432

F. W. Wang, W. H. Grant, J. H. Flynn, and B. Dickens

The photodimers formed by polycyclic aromatic hydrocarbons and their derivatives can be photodissociated to the original monomers. When the photodimer is held in a rigid matrix, the dimer can be reformed efficiently because the two monomers are held in the correct relationship for photodimerization. Since both the monomer and dimer states are stable at room temperature, a system with such a photodimer embedded in a matrix is attractive for reversible phase holographic recording with nondestructive readout.

Glassy polymers such as poly(methyl methacrylate) are good prospective candidates for the matrix material. To obtain a system suitable for holographic recording, however, dimers with suitably high solubility and with appropriate reorientation and diffusion characteristics in the matrix must be found, and the matrix must be shown to be sufficiently immutable under the conditions of use.

We are measuring the photophysical characteristics of some photodimers, such as dianthracene, and the kinetics of their photodissociation and photodimerization in poly(methyl methacrylate). Such measurements will not only contribute to holographic recording applications but will also lead to a better understanding of the relaxation processes in glassy polymers.

Measurement of Additive Diffusion by Fluorimetry

Subtask 16 of Task 15432

F. W. Wang and S. A. Svendsen[1]

[1] Guest Worker, Norwegian Food Research Institute

Antioxidants and other additives are added to polyolefins and other plastics to improve the useful properties and to extend the service life of plastics by preventing or retarding degradation. The effectiveness of these additives depends not only on their chemical properties but also on their ability to remain in the plastics throughout the intended lifetime under various end-use conditions. The basic physical quantities which control the retention of additives in plastics are their diffusion coefficients and solubilities. Thus, measurements of diffusion coefficients and solubilities are important for effective design of additive-polymer systems.

We have carried out, by fluorimetry, both extraction experiments and concentration-profile experiments to determine the diffusion coefficients of additives in low-density polyethylene.

In an extraction experiment, a plane sheet of polymer with uniform concentration of a fluorescent additive is immersed in a limited amount of well-stirred solvent. Then, the amount of the additive extracted by the solvent is determined at various times by fluorimetry. The diffusion coefficients of methyl 1-pyrenebutyrate and 1,10-bis-(1-pyrene)decane have been determined from extraction experiments.

We have used the concentration profile experiment to measure the diffusion of N,N'-diphenyl-p-phenylene-diamine (DPPD) from low-density polyethylene (LDPE) into n-propanol. A right-cylindrical rod of LDPE containing 0.1% by weight of DPPD was immersed in a large quantity of well-stirred n-propanol. As time passed DPPD diffused from the cylindrical rod into n-propanol. At the end of an experiment, the cylindrical rod was cut in the transverse direction with a microtome into circular discs of 20 μm thickness, and the concentration of DPPD in each disc was determined by fluorimetry. In this way we obtain the concentration profile of DPPD in the cylindrical rod after a fixed length of time. We are determining from this profile the diffusion coefficient of DPPD in LDPE.

In a similar experiment, we expose one end of a right-cylindrical rod made of LDPE to a well-stirred, concentrated solution of methyl 1-pyrenbutyrate in nonane. After a fixed length of time, we sectioned the cylindrical rod to determine by fluorimetry the concentration profile of methyl 1-pyrenebutyrate in the cylindrical rod. We are currently evaluating from this profile the diffusion coefficient of methyl 1-pyrenebutyrate in LDPE.

Migration of Low Molecular Weight Materials in Polymers Under Simultaneous Swelling Conditions

Subtask 17 of Task 15432

C. M. Guttman and S. S. Chang

Additives are placed in polymer films to enhance their properties, improving the polymer's chemical stability as well as the polymers mechanical properties. The loss of the additives from the polymer film into liquids in contact with the polymers not only cause degradation of the film's properties but also often contaminate the liquids causing uncertain health hazards. Thus, the loss of additives out of polymer films is an important area of study.

In earlier work in this laboratory Chang and coworkers have shown that the mass loss of an additive from a semicrystalline polymer into a solvent that swells the polymer does not obey Fick's law. They found that at early times of the extraction experiment, the amount of the additive extracted into the solution, M(t), increases as the square root of time, $t^{1/2}$. At intermediate times, M(t) increases more rapidly (almost linearly) with time. Finally, at later times, M(t) again increase like $t^{1/2}$ before the final approach to equilibrium. The diffusion coefficient at long times is found to be much larger than that observed at earlier times. Mass loss of additives from polymers into solvents which do not swell the polymer were found to follow normal Fickian behavior.

Current work is directed at the development of a theoretical model to explain this phenomena. The model being developed relates the non-Fickian migrant loss behavior to the non-Fickian sorption behavior. In particular we assume that the migrant diffuses with diffusion constant D_1 in the swollen region and with diffusion constant D_2 in the unswollen region. D_1 is greater than D_2. We assume that the swelling front is sharp and moves proportional to time (type two diffusion). Thus, it is necessary to solve the one dimensional diffusion equation in which there are two regions each having a different diffusion constant and in which the width of each of the regions changes as a function of time.

Exact analytical solutions for such a problem have so far not been possible. However, asymptotic solutions for very short time and for very long times show the limiting behavior seen in the experiments. Furthermore, an approximate analytical solution has been produced which shows most of the general features of the experimental data of Chang. In these studies the velocity of swelling was estimated from swelling data on polyethylene obtained by Rodgers et al. and D_1 and D_2 obtained from the data of Chang. Currently, a numerical solution to the problem is being undertaken.

Preliminary work on the simultaneous swelling and diffusion of small molecules in rubbers has recently been undertaken in connection with studies on the development of models for permeation of hazardous materials through protective clothing. Models of simultaneous swelling and diffusion in rubbery materials which allow one to estimate so called breakthrough times and asymptotic steady state permeations from properties of the polymer, the diffusant and the swelling agent have been proposed.

Self-Diffusion in Concentrated Polymer Solutions Measured by Fluorescence Recovery After Photobleaching

Subtask 18 of Task 15432

F. W. Wang, E.-S. Wu[1], and R. E. Lowry

[1]Physics Department, University of Maryland,
Baltimore County, Catonsville, MD

A polystyrene polymer of narrow molecular weight distribution has been fluorescently labeled with nitrobenzoxadiazole (NBD). The self-diffusion coefficient of NBD-labeled polystyrene in polystyrene-diethyl phthalate solutions has been measured by the method of fluorescence recovery after photobleaching (FRAP).

In the FRAP method, one uses high intensity illumination to deplete by photobleaching the observed volume element of chromophore-labeled chain molecules. After the bleaching pulse, the diffusion of unbleached chromophore-labeled chain molecules into the bleached volume element is observed with low intensity illumination. From the time constant for the recovery of the original fluorescence intensity, the diffusion coefficient can be obtained. The FRAP method can be used to measure diffusion coefficients in the range 10^{-11} to 10^{-6} cm^2/s.

We have found that for the NBD-labeled polystyrene with a molecular weight of 110,000, in the semi-dilute concentration region from 0.07 g/ml to 0.3 g/ml, the dependence of the self-diffusion coefficient on polymer concentration is in good agreement with the predictions of scaling and reptation theories. Recently we have labeled with NBD a circular polystyrene polymer. In collaboration with Dr. G. B. McKenna, we plan to measure by the FRAP method the self-diffusion of circular polystyrene polymers of various molecular weights.

BLENDS PROCESSING
Task 15433

Blends are a relatively new commercial development which represent one of the most rapidly growing fields in the U.S. synthetic polymer industry. Blending two or more polymers provides an inexpensive means of developing materials with improved properties and performance. By blending existing polymers, industry can avoid the expense of both new synthesis plants and new government approval tests. Further, properties can be tailored to performance specifications by blending. For reasons such as these, blends have already become nearly 20 percent of the U.S. production. Their use as engineering materials is projected to triple between 1982 and 1987.

There is strong industrial interest with many companies involved. General Electric has formed a new blends center and Exxon has sent a Research Associate to the Polymers Division to work on blends. In response to expressions of need from the plastics community, the Society of Plastics Engineers, Inc., together with its Engineering Properties and Structure Division and the National Bureau of Standards (NBS), have agreed to institute a joint program to provide data on the thermodynamics and nonequilibrium phase behavior of polymer blends. NBS will be responsible for the overall guidance of the technical aspects of the program with the aim of assuring reliability of the data evaluations, and will provide a center for coordination with other data compilation centers.

A characteristic of most blends is that they spontaneously separate into phases of different compositions. This phase separation markedly affects the useful physical properties. Industrial development of blends is hindered by an inadequate knowledge of the fundamental factors that govern the kinetics of phase separation during processing. Proper process control requires a knowledge and understanding of phase separation kinetics which are dependent on diffusional processes, interfacial phenomena, and the underlying thermodynamics. The activities of this task are focused on measurement methods, data, predictive models, and general theoretical descriptions that will form a scientific basis for optimizing control of blend processing.

NBS has five experimental facilities which, taken as a whole, represent a unique combination of tools for the study of phase separation kinetics in polymer blends: small-angle neutron scattering (SANS), Forced Rayleigh Scattering (FRS), small-angle x-ray scattering (SAXS), fluorescence energy transfer techniques, and electron microscopy. The only other SANS facility in the United States is at Oak Ridge; there are only two other FRS instruments in the world being used to study polymeric systems; fluorescence methods are relatively new and unexploited. After adding the two-dimensional x-ray detector (1984), the NBS SAXS facility will be one of the finest in the world. NBS possesses state-of-the-art facilities in imaging and analytical electron microscopy.

Polymer Blends Containing One Crystallizable Component

Subtask 1 of Task 15433

R. M. Briber and F. A. Khoury

The blending of polymers to produce mixtures whose fine structures can be appropriately controlled by varying the composition, and/or the thermal conditions used in processing, has been receiving considerable attention in recent years as a method for producing materials that can be tailored to best advantage for particular end uses. The achievement of the latter goal is governed by the miscibility (compatibility) of different polymer species, the phase separation behavior of the blends, and the extent to which phase separation can be exploited to control the fine structure (morphology) and hence the properties of the blends.

Due to the intrinsically low entropy of mixing of two components consisting of long chains, blends of compatible polymers are relatively rare. The existence of such blends consisting of either two non-crystallizable polymers, or two crystallizable components, or only one crystallizable component has, however, been reported. The study of the phase separation behavior, morphology and properties of blends of compatible polymers is a logical starting point for developing an understanding of the factors which determine and govern the compatibility or incompatibility of mixtures of different polymers.

The two-component polymer blend system we are currently studying consists of one crystallizable component, namely poly(vinylidene fluoride) (PVF_2) with M_n=47000, M_w/M_n=2.7. The non-crystallizable component is atactic poly(ethylacrylate) (PEA) with M_n=29000, M_w/M_n=2.4.

Optical microscopy has been used to outline two main features of the phase diagram of PVF_2/PEA blends. First the cloud point curve which defines the high temperature (i.e. above the melting point of PVF_2) liquid-liquid phase separation behavior of the blends has been determined. For this purpose a photodiode was substituted for one of the eye-pieces of the binocular microscope to monitor the turbidity of the samples as they were heated in a hot stage at a rate of 0.2°/min. Second, the melting point curve of the PVF_2 crystallized upon cooling the blends from the isotropic liquid phase was established.

PVF_2 and PEA blends form a single phase (compatible) melt at compositions of ≤50% (by weight) of PVF_2. Upon heating to higher temperatures i.e. above the melting point of PVF_2, the melts exhibit phase separation. This phase separation occurs at between 0 °C and 50 °C above the melting of the PVF_2 component as the content of the latter is decreased from 50% to 10%. The cloud point curve which depicts this behavior intersects the observed melting point curve of the PVF_2 component in the blends at a PVF_2 content of about 50% (corresponding temperature ~180 °C). No isotropic melt phase has been observed in blends containing 60% PVF_2 or more.

Optical microscopy has also been used to examine the morphology of the PVF_2 crystallized at different temperatures from single phase melts of blends containing <50% PVF_2. Spherulites of both the α and γ crystal forms of PVF_2 were observed in all the blends. The α-spherulites were predominate at the lower crystallization temperatures. These spherulites exhibit 'concentric ring' extinction patterns when examined between crossed polarizers indicating that the radiating lamellae in the spherulites are twisted. In addition to the fact that the twist period increased with crystallization temperature at constant blend composition, comparison of the twist period in α-spherulites formed in different blends revealed that for the same crystallization temperature the period is larger the lower the PVF_2 content of the blend. The temperature and composition dependence of the radial growth rate of α-spherulites have been determined as a prelude to a detailed analysis of the kinetics of the spherulitic cyrstallization of the PVF_2 in the blends. The γ spherulites which occur in larger profusion at the higher crystallization temperatures are of two types. One type grows as such, i.e. directly in the γ crystalline form. The other γ-spherulites are α-spherulites which have undergone an isothermal solid-solid α-γ crystal transformation during the dwell of the specimens at the crystallization temperature. This type of transformation has been previously observed in pure PVF_2 but at higher temperatures.

Current and projected work on the PVF_2/PEA blends fall into two main areas: (1) Concerning the liquid-liquid phase separation behavior of the blends, the polymer-polymer interaction parameter, χ, will be determined from melting point depression data of the PVF_2 in blends of different compositions (<50% PVF_2). In addition, scattering techniques (light or possibly x-ray) will be used to examine the kinetics of the phase separation process. (2) Three aspects of the crystallization of the PVF_2 in the blends will be examined. First, morphological details of the PVF_2 spherulites formed from one-phase melts will be determined using electron microscopy and small angle x-ray diffraction. Second, the kinetics of spherulite growth will be analyzed. Third, the effect of crystallizing the PVF_2 from phase separated melts on the morphology of this polymer and the texture of the blends will be investigated.

Small Angle Neutron Scattering from a Polyurethane Block Copolymer

Subtask 2 of Task 15433

C. C. Han, J. A. Miller[1] and S. L. Cooper[1]

[1]University of Wisconsin

Small angle neutron scattering experiments were performed on a series of polyether polyurethane block copolymers. The samples possessed the same chemical composition, but differed in the percentage of polyether soft segments that were completely deuterolabelled. At about 30% of deuteration of polyether, interphase scattering was greatly suppressed. The coherent scattering is dominated by the interchain scattering. The single chain scattering functions extracted from the scattering data yield a radius of gyration for the soft segment that is substantially larger than that reported for the polyether homopolymer in theta solvent. Thus the soft segment chains in this lamellar block copolymer are in a somewhat extended conformation. Experimentally, it was found that the technique of matching the interphase contrast yielded the single chain scattering function with greater accuracy than did the subtraction method.

Neutron Cloud Points and Concentration Fluctuations of Polymer Blends

Subtask 3 of Task 15433

C. C. Han, H. Yang[2], M. Shibayama[2], and R. S. Stein[2]

[2]University of Massachusetts

Cloud points were observed in the blends of deuterated polystyrene and hydrogeneous poly(vinyl methyl ether) by means of a temperature scanning small angle neutron scattering technique. The scattering function in the miscible region can be described by the random phase approximation results calculated by P. G. deGennes. This scattering function can also be expressed in the Ornstein-Zernike form in the small q region. A correlation length and spinodal point can then be determined from this critical fluctuation approach.

Molecular Weight Dependence of Phase Diagram and Critical Fluctuation of DPS/PVME Blends

Subtask 4 of Task 15433

C. C. Han, M. Okada[3], Q. Tran-Cong[4], Y. Muroga[5] and B. J. Bauer

[3]Tokyo Institute of Technology; [4]Kyoto University; [5]Nagoya University

The small angle neutron scattering technique is used in this study to obtain both the cloud point curve and the spinodal curve for a series of deuterated polystyrene poly(vinyl methyl ether) blends. Temperature and composition dependence of correlation length in the miscible region can be measured. This together with the extrapolated scattering intensity at $q \rightarrow o$ as a function of reduced temperature can be compared with critical exponents of mean field type. The molecular weight dependence of fluctuation length when it is smaller than the polymer dimension is of special interest. Also, the temperature-molecular weight-concentration dependence of the binary interaction parameter χ will be measured.

Phase Separation Kinetics by Temperature Jump Light Scattering Measurement

Subtask 5 of Task 15433

C. C. Han, M. Okada[3], Y. Muroga[5], and Q. Tran-Cong[4]

A computer controlled light scattering photometer has been fitted with a temperature controlled film sample stage. This is designed to study the phase separation kinetics of polymer blends through temperature jump into the immiscible region and then measure the growth rate of spinodal decomposition through the computerized scanning photometer. Deuterated polystyrene-poly(vinyl methyl ether) system is currently being measured. The initial time and q-dependence of scattering intensity will be compared with linearized theory of Cahn-Hillard type. Also, this kinetic measurement of the same system will be compared with the static measurement from SANS.

Forced Rayleigh Scattering and Dynamic Light Scattering Study of Binary and Ternary Blend Systems

Subtask 6 of Task 15433

C. C. Han, Q. Tran-Cong[4], M. Okada[3], Y. Muroga[5], and T. Chang[1]

[1]University of Wisconsin, [3]Tokyo Inst. of Technology, [4]Kyoto University, [5]Nagoya University

The forced Rayleigh scattering instrument constructed last year is currently being used to study diffusion coefficients of binary and ternary blends system in the miscible region. For the ternary system which consists of the polymers and solvent, the results will be compared to the dynamic light scattering measurements. Concentration and temperature scaling of diffusion coefficient will be examined and compared with homopolymer solutions in the semidilute region.

Equilibrium Phase Compositions of Heterogeneous Random Copolymers

Subtask 7 of Task 15433

B. J. Bauer

Random copolymers do not consist of molecules all having the exact same composition. Rather they have a distribution of composition between the limits of two pure homopolymers. Such a mixture has to be treated as a blend of very many components. The Flory-Huggins theory of polymer solutions has been used to calculate the equilibrium conditions for these heterogeneous copolymers. A computer program has been written to find a numerical solution to the problem. For any type of distribution the number of phases, volumes of each phase and composition of each phase is computed as a function of chain length and the interaction parameter.

Phase diagrams have been generated based on several model distributions and on the theoretical distribution resulting from a butadiene-acrylonitrile copolymerization. As the chain length and interaction parameter increase many phases are in equilibrium. The initial calculations assumed a monodisperse molecular weight but the technique is capable of accounting for molecular weight distribution and added solvent.

Synthesis and Characterization of High Molecular Weight Polyvinylmethyl Ether

Subtask 8 of Task 15433

B. J. Bauer and B. F. Hanley[6]

[6]University of Minnesota

There is growing interest in poly(vinyl methyl ether) (PVME) because it forms compatable blends with polystyrene. The numerous studies of this system have used relatively low molecular weight PVME. It is generally obtained commercially and is of unknown purity.

Several hundred grams of PVME has been synthesized. Cationic polymerization of vinyl methyl ether with Boron trifluoride diethyl ether catalyst is carried out in a toluene solution at -78 °C. Rigorous drying techniques are necessary to obtain the high molecular weight. The PVME was fractionated to obtain samples of narrow molecular weight distribution with a range of average molecular weights.

The fractions were characterized by gel permeation chromatography, intrinsic viscosity and light scattering. The molecular weight of the samples range from $\sim 10^5$ to 1.5×10^6 Daltons with polydispersity index as low as 1.3. Empirical Mark-Houwink constants were determined for the polymer in methyl ethyl ketone and tetrahydrofuran, the latter being useful for the analysis of gel permeation chromatography.

A Universal Coexistence Curve for Polymer Solutions

Subtask 9 of Task 15433

I. C. Sanchez and F. L. McCrackin

Coexistence (COEX) curves for binary polymer/solvent solutions are asymmetric when volume fraction is used as the concentration variable. In principle, if the appropriate concentration variable (order parameter) is chosen, binary liquid COEX curves should be nearly symmetrical and satisfy a simple scaling law of the form $|P-P_c| \sim \varepsilon^\beta$ where P is the correct order parameter, P_c is the critical value of the order parameter, $\varepsilon \equiv (T_c-T)/T_c$, T_c is the critical temperature, and β is a universal exponent. COEX curves for polystyrene/methylcyclohexane solutions can be symmetrized by a simple transformation of variables; in the new dimensionless variable ψ, all of the COEX data satisfy a universal scaling law:

$$|\psi-\psi_c| = \psi_o(\varepsilon N^{0.313})^{\beta}$$

where N is the degree of polymerization and ψ_c and ψ_o are constants independent of N. The experimental value of the critical exponent β (0.327±0.002) agrees well with recent renormalization group calculations for the Ising model. The exponent on N(0.102 ±0.002) may be universal and should be compared with its mean-field value of 1/4; a calculation of its non-classical value remains a challenging theoretical problem.

Block Copolymers with Lamellar Morphology: Chain Dimensions in Directions Parallel and Perpendicular to the Lamellae

Subtask 10 of Task 15433

E. A. Di Marzio and I. C. Sanchez

In block copolymers chains are stretched out in the direction perpendicular to the planes of the lamellae. The packing entropy contributes a term that results in a shrinking in the transverse dimension. Quantitative estimates are made. The result is a substantial improvement over classical results which predict a negligible shrinkage in the transverse dimension. The thicknesses of the lamellae are shown to vary as the 2/3 power of the molecular weight. The effect of adding solvent and homopolymers is being examined. Block copolymers can be used to stabilize polymer blends.

Classification of Structure-Inducing Transitions in Polymers
Subtask 11 of Task 15433

E. A. Di Marzio

Phase transitions in polymers constitute a rich subject area. There are more transitions occurring in polymer systems than in any other. Four transitions unique to isolated polymers are 1) the helix-random coil transition, 2) the collapse transition, 3) adsorption onto a surface, 4) polymerization. Transitions which occur among collections of molecules also are richly represented in polymers. Much structure occurs in liquid crystals. Polymeric thermotropic liquid crystals of the nematic, cholesteric, and smectic type exist. Each of the lyotropic liquid crystals also have polymeric representatives. When we add to the above transitions those common to all materials such as crystallization, glassification, and the liquid-liquid transitions we begin to appreciate the richness of the subject. These transitions can be made to couple to one another giving a hierarchy of structures involving feedback and control. An attempt is being made to describe each of the transitions with a simple mathematical treatment which captures the physical basis of the transition. Also, the effect of chemistry on phase transitions is being studied. These studies will facilitate treatments which couple the various transitions to one another.

Phase transitions are useful to processing science because a slight change in one of the control variables (examples: temperature, pressure, affinity, pH, ionic strength, shear rate, strain) can result in sudden appearance of structure. The plethora of structure-inducing phase transitions in polymer systems warrants study.

Weighted Random Walks and Polymer Chain Configurations
Subtask 12 of Task 15433

R. J. Rubin

In discrete lattice random walk models of adsorption of polymer chains at solution surfaces, polymer chain configurations which penetrate the surface must be given zero weight, while the weight of each of the remaining configurations is increased according to the number of visits of the configuration to the surface. There is a critical value of the energy weight per visit to the surface at which the sum of the weighted configuration probabilities is normalized (as was the sum of the unweighted probabilities). In a previous investigation of the case of a plane surface, we have compared properties of this adsorption model at the critical weighting value of the energy with properties of the analogous model at a reflecting surface (a model in which the sum of the configuration probabilities is also normalized). There are significant differences between these two discrete models, in contrast to the continuum random flight model discussed by deGennes where the analogous models become identical.

In a further investigation of the differences and similarities between the discrete lattice random walk model of adsorption and the corresponding continuum random flight model, we are studying a discrete random walk model of adsorption of a flexible polymer chain on a long rigid-rod molecule [1] at its critical weighting value of the energy. In the case of the discrete random walk, we have already found differences between properties of the adsorption model and the analogous model with reflecting boundary conditions.

[1] R. J. Rubin, J. Chem. Phys. 44: 2130; 1966.

Nanosecond Fluorimeter for Measurements of Polymer Phase Diagrams
Subtask 13 of Task 15433

F. W. Wang, F. L. McCrackin, J. D. Barnes, and W. H. Grant

The nanosecond fluorimeter for measurements of polymer phase diagrams by the energy transfer technique has been installed by the vendor and interfaced to a computer. The interface hardware that has been installed permits changing specimens, performing lamp intensity calibrations, measuring blank specimens, and changing the excitation wavelength without operator intervention. New computer programs are being written to utilize these capabilities. This is expected to boost productivity because a complete series of fluorescence decay experiments may require upwards of 12 hours.

Digital Camera for Small-Angle X-ray Scattering
Subtask 14 of Task 15433

J. D. Barnes

The functional layout of the NBS 10-meter small-angle x-ray scattering camera is shown in Figure 1.

Activities related to development of the new facility for small-angle x-ray scattering can be divided into the following areas:

1. Site preparation
2. Camera design and construction
    a. X-ray source
    b. Monochromator and beam monitor
    c. Beam path (including specimen stage)
    d. Computer interfacing for data acquisition and control
3. Software development
    a. Data acquisition
    b. Camera control
    c. Data analysis and display

Initial site preparation is essentially complete, with installation of the x-ray generator expected to be complete at the end of July 1984. The x-ray generator is mounted on a rotatable table that allows selection of monochromatic x-radiation of various wavelengths. The graphite monochromator has been obtained and will be installed once the x-ray generator is in place.

Procurement of the beam monitoring electronics and the control interface components for the beam path is nearly complete. Design work on major beam path components, including the vacuum chambers and support structures, is underway and these items will be constructed in the NBS shops at the beginning of FY 1985.

The data acquisition and control computer and the color graphics display system have been acquired and installed. Software for display and analysis of small-angle scattering data has been obtained from the NBS Reactor Division. Because of differences in display hardware it was necessary to revise much of this software in order to adapt it to our equipment. The resulting display system is much more rapid and interactive than its prototype. We have, however, retained compatability with respect to data structures and data analysis algorithms so that data from the x-ray and neutron small angle scattering cameras may be analyzed at both sites. Our analysis and display system is currently operational, thus allowing some modeling studies to proceed.

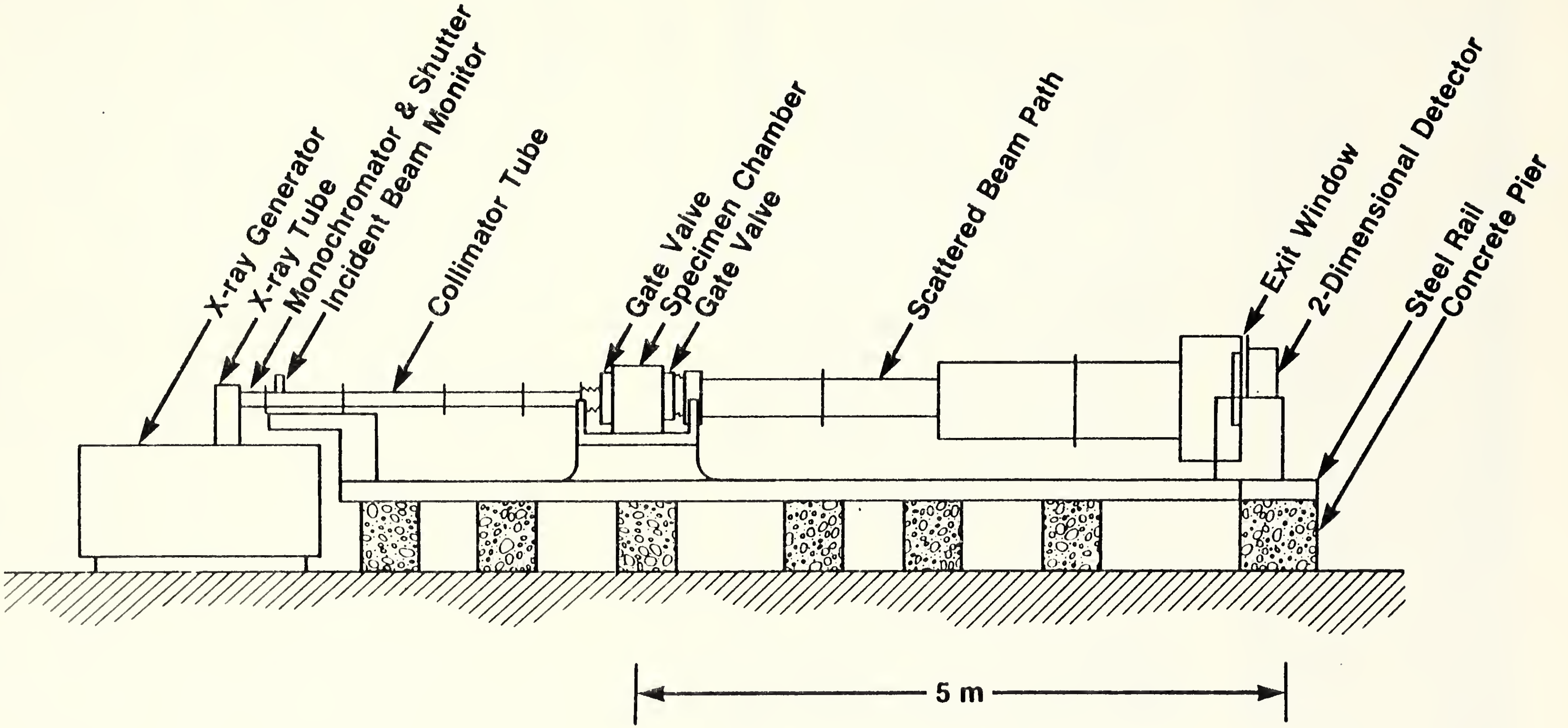
Further work is underway to implement additional software for contour plotting, 3-dimensional plotting, non-linear least squares fitting, and resolution modeling.

The manufacturer of the two-dimensional position-sensitive detector has experienced turnovers in key skilled personnel. This has resulted in a delay of approximately six months in delivery of this component. The detector has, however, been built and is currently being tuned by the vendor. Delivery is anticipated during July 1984.

Software for data acquisition will be written as soon as we are able to interface the detector to the data acquisition computer. Substantial software development work is required because of differences in the data acquisition hardware and in the computer operating systems between our data acquisition system and that being used on the small-angle neutron scattering camera in the Reactor Division.

Calibration of the camera and collection of small-angle x-ray data from polymer specimens is expected to begin in January 1985.

Small Angle X-ray Scattering Facility



TESTS, STANDARDS AND CHARACTERIZATION FOR MANUFACTURING AND DURABILITY OF DENTAL AND MEDICAL MATERIALS
Task 15435

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 efforts on diagnostic systems or therapeutic equipment exists, this too lies within the realm of feasible activity.

Materials research efforts support development of materials and techniques which will provide adhesion and increased durability and wear resistance of composite restoratives, decrease marginal microleakage, and add to the knowledge available for the development and use of less costly alternatives to gold casting alloys and dental porcelains. The understanding of the structure and physical chemistry of calcium phosphates as they relate to biological systems is being advanced for the development of new or improved preventive and restorative stomatological treatments (applications for other than oral diseases are also considered). New cements with improved properties and biocompatibility have potential as luting agents, endodontic sealers and temporary restoratives. Methods of modifying surgical bone cement to improve durability, radiopacity, and performance of bone cement-implant systems are being pursued.

Dental Composite and Sealant Chemistry and Related Developments
Subtask 1 of Task 15435

J. M. Antonucci, G. M. Brauer, R. L. Bowen, J. W. Stansbury, N. W. Rupp and R. W. Penn[1]

Certain critical properties (e.g. hardness, wear resistance, etc.) of polymerized dental composites are determined to a large extent by the ultimate crosslink density, glass transition temperature (T_g) and solubility parameter (u) of the organic matrix. Previous work in these laboratories demonstrated that polymerization at 80°C rather than 37°C yields composites with improved mechanical properties, and better resistance to the softening effects of a simulated oral environment. The improved nature of these heat-cured composites was ascribed to an increase in the degree of conversion of vinyl groups resulting in a material of higher crosslink density and T_g. Previous work also demonstrated the efficacy of small amounts of a multifunctional chain transfer agent such as pentaerythritol tetra(3-mercaptopropionate), PETMP, in reducing the residual vinyl content of polymerized dental resins. PETMP, as was noted before, also improves the esthetics and color stability of resin based composites.

This laboratory has now shown that for certain resin systems (e.g. BIS-GMA, non-hydroxylated homologs of BIS-GMA, a highly fluorinated prepolymer monomer -PFMA) the effect of small amounts of PETMP is also to enhance the diametral tensile strength (DTS) of the corresponding composites. That is, a good correlation exists between conversion of vinyl groups and DTS within a given resin system. However, when employed with a rather stiff prepolymer monomer (BIS-GMA/NCO, which is a polymeric urethane

---

[1] See end of Task 15435 for affiliations of individual scientists.

derivative of BIS-GMA in a conventional diluent monomer) surprisingly no improvement in double bond conversion or DTS was noted. The bulky nature of PETMP or its reaction products with the diluent monomer may operate to limit the diffusion of these moieties to the reactive sites of BIS-GMA-/NCO.

In the area of low surface energy resins a translucent composite based on PFMA resin systems and fused quartz has been developed. In addition to the excellent esthetics suitable for anterior use these composites exhibited excellent mechanical strength and low water sorption.

One of the factors considered to be important in the application of composite dental restorative materials as well as of certain adhesive materials is the degree of shrinkage which occurs during polymerization. In order to measure this shrinkage a simple mercury filled dilatometer system was assembled. The dilatometer itself is constructed from a spherical glass joint which is ground flat and covered by a flat quartz plate. The plate is held in place by the spring clamp normally used to assemble the joints. The stem of the joint is bent into a "U" tube and filled with mercury. The mercury is drawn up into the "U" tube by light vacuum and the sample is inserted by sticking it to the inside of the quartz plate. When the vacuum is removed mercury flows down to fill the joint and surround the sample. Any trapped air leaks out between the plate and the ground surface of the joint. The high surface tension of mercury prevents it from leaking. Volume changes are monitored using a linear variable differential transformer whose core is attached to a poly(tetrafluoroethylene) slug which floats on the surface of the mercury in the "U" tube.

The system has a resolution of about 10^{-5} cc. This is sufficient to allow us to measure shrinkages of 2 to 5% with a standard deviation of 0.1%.

Dental Adhesion Research

Subtask 2 of Task 15435

R. L. Bowen, G. M. Brauer, J. M. Antonucci, J. W. Stansbury, D. N. Misra, and E. Cobb

Effective bonding to tooth enamel is presently achieved by means of acid-etch treatments. Similar treatments for bonding to dentin have proved ineffective, and are often contra-indicated. Adhesive systems and methodologies that would bond effectively not only to dentin but also to enamel without the necessity of removing sound hard tissue are being investigated.

Certain alkyl cyanoacrylates, which polymerize anionically at ambient temperatures, had been shown to initially form strong bonds to dentin. However, these bonds weakened significantly on exposure to water. In an effort to stabilize and maintain the good intiial bond strength to dentin, a functional alkyl cyanoacrylate, which is capable of crosslinking with itself and/or copolymerizing with dental resins has been synthesized. Prelinimary studies have shown this cyanoacrylate to be a highly reactive monomer. Evaluation of its bonding potential to dentin will be carried out in the near future.

Another unique approach for a tooth-structure conserving bonding procedure has recently been developed which utilizes brief applications of a cleanser mordant aqueous solution of ferric oxalate, a surface-active comonomer and a coupling agent. The surface-active comonomer is either NTG-GMA, or NPG-GMA, the adducts of glycidyl methacrylate with N(p-tolyl) glycine and N(phenyl)glycine, respectively. The coupling agent is PMDM, the diadduct of pyromellitic anhydride and 2-hydroxyethyl methacrylate. Scanning electron microscopy evidence shows that the iron oxalate solution alters the surface layer. The surface-active comonomer and the coupling agent then provide molecules which are bound to the altered surface and yield the capability of copolymerizing with subsequently applied resin of the composite material. With enamel surface the average tensile bond strength was 13.5 MPa, about the same as obtained with the acid-etch technique. With dentin, tensile bond strength averaged 13.1 MPa (range 10.2 to 18.2 MPa). In addition to an adhesive mode of failure, the fractured surfaces exhibited frequent cohesive failure in the composite and occasional cohesive failure in dentin. The possibility of substituting NPG for NTG-GMA or NPG-GMA was investigated. Bond strengths using NPG were only slightly lower and the expected improved stability of NPG renders it a viable candidate for use in commerical products. The biocompatibility of this promising adhesive bonding system is undergoing evaluation prior to clinical trials. Tests such as human red blood cell hemolysis, mouse acute oral toxicity, (lg/Kg), mouse fibroblast cloning efficiency and the Ames mutagenecity test were conducted. Results indicate that components are neither toxic nor mutagenic.

Dental Cements
Subtask 3 of Task 15435

G. M. Brauer, J. M. Antonucci and J. W. Stansbury

The hexyl vanillate (HV) or ethyl syringate (EHS), ethoxybenzoic acid (EBA), ZnO cements developed in NBS laboratories have higher strength and lower solubility than the commonly used zinc oxide-eugenol (ZOE) or EBA cements. They do not inhibit polymerization and are compatible with acrylic resins and composites. On modification of the HV-EBA liquid by incorporating methacrylate monomers and by adding silanized glass to the powder in combination with suitable initiator-accelerator systems, powder-liquid mixes with good working properties that harden in 5 to 10 minutes are obtained. The biocompatibility of these cements appears to be excellent with pulp irritation studies eliciting results similar or better than those of ZOE type materials.

Further improvement of these cements was obtained by coating of a portion of the zinc oxide powder with propionic acid, preferably in a concentration of not more than 2%. Addition of the propionic acid improves working properties of the mixes, decreases setting time, and allows the incorporation of higher concentrations of HV into chemically useful formulations. It also reduces brittleness of HV-EBA and EHS-HV-EBA cements. Dental luting agents of standard consistency with film thickness as low as 8 μm can be prepared. On addition of plasticizing agents, e.g. zinc undecylate, flexible materials can be obtained, these may be useful as tissue packs.

Incorporation of a leachable fluoride without lowering the physical properties of the cement may yield a caries reducing material. Thus, cements with sodium fluoride or disodium monofluoro phosphate were evaluated. Cements containing the latter ingredient were brittle. HV-EHS-EBA cements with 0.5% NaF had adequate strength. Since there was an excessive leaching of fluoride ions into water for prolonged time periods, cements with lower fluoride content are being evaluated.

ZOE cements and temporary restoratives do not bond to composites or metal in an aqueous environment. The HV-EBA or HV-EHS-EBA as well as their cement composites adhere well to non-precious metals, composite resins and porcelain. The joined specimens break cohesively close to the tensile strength of the cement. Highest bond strength up to 15.6 MPa are obtained with cement-composites. Adhesion of these cements to stainless steel or porcelain is equal to or better than that of ionomer cements. With pretreatment their adhesion to enamel or dentin is equal to that of the latter cements.

Studies conducted at Northwestern University School of Dentistry indicate that the HV-EBA-ZnO formulations appear most useful as endodontic sealing materials.

In spite of their relatively poor durability, commercial dental cements are widely used in a variety of applications, e.g. luting agents for fixed restorations and orthodontic appliances, as a base under permanent restorations to insulate against thermal and chemical shock, as root canal filling and pulp capping agents; and as temporary and intermediate restoratives. Cements in current use lack toughness (i.e. they have propensity to brittle failure) and hydrolytic stability (i.e. they tend to erode excessively in the oral environment). In previous work we have shown that a new versatile class of cements based on the reaction of dimer (DA) or trimer acids (TA) with polyvalent metal bases (e.g. ZnO, MgO, Ca(OH) etc.) is feasible.

Some of these cements (e.g. $Ca(OH)_2$-DA) are characterized by their non-brittle nature under moderate rates of deformation (i.e. they display viscoelastic behavior similar to thermoplastic polymers). At higher rates of deformation brittle failure occurs. DA or TA cements based only on MgO as a base exhibit brittle failure both at moderate and high rates of deformation. Using both $Ca(OH)_2$ and MgO as the base component yields cements of intermediate rheological properties. The rheological behavior of these cements can be further modified by the addition of mineral and/or polymeric fillers.

Wear Mechanisms and Durability of Dental Composite Materials

Subtask 4 of Task 15435

J. E. McKinney, N. W. Rupp, and J. M. Antonucci, and W. Wu

Microdefect analysis on *in vivo* worn posterior composite restorations reveal chemical interaction with the oral environment resulting in extensive damage on the surfaces of the restorations. The objective of this work is to determine the *in vivo* degradation mechanism of dental composites used in occlusal applications and to use this information as a basis to improve these materials. Past work has shown that *in vitro* (pin and disc) wear on composite specimens preconditioned for one week in certain organic solvents designated by the FDA as food simulating liquids often was enhanced considerably over those stored in inert media for the same period of time. The enhanced degradation of the surface is attributed to the softening of the undercured polymer matrix by the preconditioning fluid. Maximum wear is obtained when the solubility parameters of the polymer and preconditioning liquid are proximate.

This year attention was diverted to the study of the degradation of the other component of the composite, namely, the inorganic reinforcing filler. The large surface/volume ratio of the small filler particles makes the composites, in some cases, vulnerable to attack from oral acids and even pure water. During wear the degradation is accelerated by stress corrosion of the filler and corrosion is, in turn, accelerated by wear. The wear of pure silica filled composites were the least affected from preconditioning in water or weak acids. Many radiopaque composites, for which fillers are modified by incorporation of alkaline earth elements were found to be more sensitive to exposure in these media. For example, the wear of the strontium glass filled composite was found to be enhanced by a factor of five after preconditioning in water. Since more dentists are demanding radiopaque composites (in order to detect adjacent decay), this vulnerability imposes a serious problem to the development of durable posterior composites. No complete solution to this problem is recognized at this time.

In collaboration with the L. D. Caulk Co., Milford, DE, pin and disc wear measure were made on composites containing negative expanding (with respect to increasing temperature) glasses. These materials contain lithium and barium modified "glasses" which are semicrystalline. The barium component produces radiopacity. The unit cell of the crystalline portion expands and contracts on different axis leading to a net volume decrease with increasing temperature. The negative expansion of the glass opposes that of the polymer matrix giving an insignificant change in the composite. This result is expected to improve the durability of composite restorations.

Since these fillers are semicrystalline, their corresponding higher densities are expected to be more resistant to penetration of water and weak acids. Our preliminary wear measurements have not revealed any significant distinctions in wear from preconditioning these specimens in different fluids.

Another characteristic of these glasses is that they tend to phase separate. If the lithium component at the surface of each particle is removed by etching, the surface is roughened leading to improved mechanical coupling with the polymer matrix. Preliminary *in vivo* wear measurements on these composites revealed that etching these materials enhanced the wear resistance by a factor approximating 2.5.

Recently wear measurements have been initiated on ionomer cements. These materials have carboxylate groups which unite with polyvalent metallic cations forming a cohesive mass which will adhere to enamel. Depending on the choice of metallic cation (or salt) these restoratives may be made radiopaque. We wanted to determine if ionomer cements have potential application as posterior restoratives. Preliminary measurements indicate that although the wear resistance is as high as that for many composites, these materials are extremely brittle and often fracture during wear. In addition considerable degradation results from exposure to lactic acid, an ingredient commonly existing in the oral environment.

A scheme of measuring the oral environmental resistance of restorative dental composites was developed; the resultant resistance index R is designated to represent the softening resistance of the matrix resins against various substances existing in the oral environment. Twelve commercial dental composites have been evaluated using this method. For these three dental composites with clinical performance information available, a correlation is observed between their performance and the R rating. More clinical data are needed to fully assess the viability of the R index measurement.

Porcelain Fused to Metals (PFM) and Dental Ceramics (DC)

Subtask 5 of Task 15435

J. A. Tesk, W. deRijk, H. R. Kase, G. Widera, D. L. Menis, and R. W. Hinman

An important consideration in calculation of thermal stress compatibility is the elastic modulus of each of the materials involved and their temperature dependencies. The moduli of dental porcelains were determined to be ~70 GPa near 23°C; the moduli of three dental alloys were determined to be ~144, 172, and 192 GPa. The modulus of each material decreases by about 1% for each 100°C increase in temperature. An estimate of the microcrack density, N, shows $N \approx 3.4 \times 10^4$ cm^{-3} for dental porcelains.

Theoretical studies of thermal stress compatibility are being pursued via finite element modeling (FEM) of idealized systems. Although there will be some question of the accuracy of the calculations because of large temperature gradients coupled with viscoelastic behavior, the results are expected to clarify some points regarding the regions of development of highest thermomechanical stresses.

A FEM has been developed to study the effects of different PFM and DC materials on the stresses developed within dental cements.

The mathematical analysis has been completed on the chemical durability of experimental dental porcelains as function of the constituent oxide concentrations.

Other routes to produce dental porcelains from solutions and solids have been explored. For solutions that have exeedingly long sol-gel transition times the decomposition of misted solutions provides an alternative method for porcelain powder production. The method requires no additional grinding or processing of the frit, however the environmental impact of this production method requires further attention.

The low fusing porcelains previously produced have been further developed to produce porcelain veneers that adhere to metal (dental casting alloys) and still have a fusion temperature between 700°C and 750°C.

Dental Casting Alloys and Investments
Subtask 6 of Task 15435

J. A. Tesk, R. W. Waterstrat, W. deRijk, S. Hirano, R. W. Hinman and H. R. Kase

A simple technique has been developed for determining a castability value, C_v, for dental casting alloys. The percentage of completely cast grid segments from a polyester pattern is defined as being C_v. It is convenient, mathematically, to work with a transformed value of C_v, i.e. $C_{v,t}$, to represent C_v as a function of mold temperature, T_M, and alloy temperature T_A,

1. $C_{v,t} = a + bT_A^{1/2}T_M^2$

Where T_A = alloy casting temperature in terms of degrees of superheat above the alloy solidus temperature.

T_M = the mold temperature

Chemical analysis of the six alloys, followed by multilinear regression analysis along with an employment of equation 1 for $C_{v,t}$ has allowed a development of the first equation for effects of individual elements on the castability value, C_v, as function of mold and alloy temperature.

2. $C_{v,t} = K_0+K_i(Si)+K_2(B)+K_3[CbxSn]+K_4[Al+Be]+K_5[Mo+Mn]$

Where $K_m = f_m(T_A, T_M)$

Further work is planned to refine equation 2 and define the constants, K_m, accordingly.

A new method to determine the setting expansion of dental casting investments has been explored. This method relies on embedded strain gauges to determine dimensional changes during the setting process. This still experimental method has generated significant interest from manufacturers.

Recent work has shown that dental appliances of commerically pure titanium can be cast using a small electric arc furnace powered by an ordinary D.C. electric welder. It was found that both a magnesium oxide investment (developed in Japan) and a zirconium oxide investment (developed at the U. S. Bureau of Mines) are capable of producing excellent castings without contamination of the metal. The first clinical trials of pure titanium crowns are presently planned in collaboration with Dr. N. W. Rupp.

Dental Chemistry, Crystallography, and Preventive Treatments
Subtask 7 of Task 15435

W. E. Brown, L. C. Chow, M. Mathew, S. Takagi, M. Tung, G. L. Vogel, T. M. Gregory, C. M. Carey, B. Sieck, and C. Schreiber

Fundamental studies on the chemical properties and crystallographic structures of tooth and bone minerals and other biologically important calcium and phosphate containing compounds are conducted. The information obtained is applied to the development of improved caries preventive techniques. Work conducted under this project includes studies on topical fluoridation, mechanisms of biomineralization, caries mechanisms, calcium phosphate cements, crystal structures of biomaterials, and x-ray magnification radiography.

Work continues on the new procedure for topical fluoridation which involves treating the tooth with solutions that form dicalcium phosphate dihydrate (DCPD) in the enamel to make it more reactive towards fluoride. Another cooperative fluoride-uptake and caries-score study was carried out with investigators at NIDR using the rat model. Once again the DCPD pretreatment considerably increased the permanently-held fluoride content of teeth and produced the lowest caries score. However, due to the relatively large standard deviations, the caries score was not significantly different from the fluoride treatment alone. Our present procedure requires two treatments, DCPD-forming solution followed by fluoride solution. By incorporating into the DCPD-forming solution a complex fluoride which does not react with calcium ions, the procedure may be reduced to a single treatment. Initial laboratory results showed that SiF_6^2 ions served well for this purpose. Based on the above principle, a patent application was filed: "Composition and Methods for Topically Fluoridating and/or Mineralizing Dental Enamel".

A new procedure was developed for measuring the amount of DCPD formed in the tooth. The procedure involves the titration of a DCPD-treated tooth in a fluorostat. The ease and accuracy of this procedure should be of great value in determining the proper parameters for DCPD treatment and topical fluoridation. Progress was made in the use of the calcium phosphate cement as an endodontic filler. After a preliminary study using extracted human teeth in which improved formulations were developed, the cement is being tested in dogs. A patent application has been filed: "Combinations of Sparingly Soluble Calcium Phosphates in Slurries and Pastes as Mineralizers and Cements".

This laboratory has long advocated the view that octacalcium phosphate (OCP) participates as a precursor in the formation of tooth and bone mineral. There is growing evidence that in biological calcifications OCP is formed first, then hydrolyzes to a nonstoichiometric hydroxyapatite. A procedure was developed in our laboratory by which these two processes can be separated and studied individually to determine the effects of physiologically active components on the rates of these two mineralization processes which form tooth, bone, and pathological mineral deposits such as those in atherosclorotic plaque.

A significant step in the study of all biological mineralizations was made when it was found that the calcium and phosphate ion activities could be measured with precision in ultra-filtered serum. This will make it possible to study these parameters as functions of age of the individual, time of day, disease, diet, etc. Progress was made in establishing conditions for studying the solubility of calcium phosphates in atherosclerotic plaque. Progress was made in determining conditions for the use of calcium phosphate slurries and highly supersaturated solutions in remineralization of carious lesions.

Caries Mechanisms: The work on caries mechanisms has been expanded to include studies on four levels: (1) theroetical considerations which focus on the fact that the relative rates of diffusion of ions into and out of the lesion can be important parameters affecting the rate of caries progression, (2) bench-scale experiments using a two-compartment diffusion cell to test the major principles of the proposed caries model, (3) a computer simulation model which has produced results in close agreement with the bench scale studies and allows us to survey rapidly the effects of a large number of variables, and (4) ultramicro-analytical studies on tooth sections to establish quantitatively the events occuring within the enamel during artificially induced caries formation. Results from the above studies have produced important new insights into the factors governing the caries process.

Progress has been made on the development of cements that harden in water and form compositions nearly identical to tooth and bone mineral. A method was developed which can produce cement specimens with greater strengths and with pores if needed for bone implant applications. In collaboration with the Research Institute, a study to test the biocompatibility of the cement using animal models has been initiated. A patent application, "Combinations of Sparingly Soluble Calcium Phosphates in Slurries and Pastes as Mineralizers and Cements", was filed.

The crystallographic studies provide a structural base for understanding the chemistry of biominerals and their interactions with dental materials. Crystal structure of $Ca_2KH_7(PO_4)\cdot H_2O$ has been determined using x-ray and neutron diffraction data. Research on the structural studies of octacalcium phosphate, $Ca_8H_2(PO_4)_6\cdot 5H_2O$ and its role in biomineralization and the surface and colloidal properties of apatites continue to be a major activity.

A new study of the structural features in mineralized tissues using x-ray magnification microradiography has been initiated. X-ray magnification microradiography is a new technqiue that was developed by the National Bureau of Standards' Metallurgy Division. Considerably better resolution may be obtained by this technique than by standard contact microradiography. Preliminary studies have clearly shown images of dentin tubules and special features of carious lesions.

Clinical and Laboratory Investigation of Dental Amalgams, Composites and Glass Ionomer Cements

Subtask 8 of Task 15435

N. W. Rupp, W. deRijk, G. C. Paffenbarger, and R. W. Waterstrat

The success or failure of dental restorations can be determined only after long term, greater than two years, observations. The causes of failure relate to three categories: (1) the physical, mechanical and chemical properties of the material; (2) the operator's selection of material, cavity preparation and manipulation of the material; and (3) the patient's home care. Sorting out of the factors contributing to the durability of restorations requires a careful combination of clinical studies and laboratory analyses.

Amalgam restorations placed in our clinical study over ten years ago are continually being observed. These, along with observations of in vitro specimens made seven years ago, show an interesting correlation within our laboratory and with observations reported from other laboratories. Unrestricted amalgam specimens, 4 x 8 mm cylinders, have been stored at 60°C for six years and their length and diameter measured and changes in dimensions recorded. Currently we have the clinical data from an outside laboratory for three alloys in common with our study. The clinical study reports the deterioration of restorations directly in comparison with our yearly laboratory observations. When this data, after seven years, is plotted, there is a straight line from the fiducial reading. Clinical studies are expensive and time consuming. If the laboratory tests in a few months do predict what the long-term clinical studies finally show, then patients, dentists, and manufacturers will be saved considerable money and time.

Composite restorations placed both in vivo and in vitro are being observed for margin staining using commerical products recommended for bonding to dentin. Only those products having proof of safety to the pulp are being used in in vivo. One brand which works well in vitro has been observed in vivo. Early results are promising, however, several failures in bonding to dentin indicate technique sensitivity, so handling techniques are now being studied.

A thorough search of the literature was completed concerning potential mercury toxicity from dental amalgams in preparation for an NIDR-sponsored workshop on Biocompatibility of Metals in Dentistry. A talk was prepared and will be part of the workshop proceedings.

The in vivo evaluation of restorative composite resins with enhanced polymerization continues with patients reporting to the clinic at three month intervals for evaluation of the restorations. This study will terminate at the end of FY85.

A hydroxyapatite producing paste is being used as a therapeutic agent for the reduction of hypersensitivity of exposed dentin. A total of 16 patients participated in this study. The results of this study are currently being processed.

Improved Surgical Bone Cement
Subtask 9 of Task 15435

G. M. Brauer, J. A. Tesk, J. W. Stansbury, W. L. Wu, J. E. McKinney and R. W. Penn

A study of the effect of different inhibitors, accelerators, chain transfer and cross-linking agents in the benzoyl peroxide initiated polymerization of monomer-polymer mixes has been completed. Based on these results a series of compositions with short curing times, lower polymerization exotherms and mechanical properties that exceed those of a commerical material and surpass all requirements of the specification for bone cements have been formulated.

To improve properties efforts have been directed to replace barium sulfate as the radiopacifying agent in these cements. Methacrylates containing substituents with atoms of high atomic weight such as bromine, iodine or zinc are being considered. Such monomers, if compatible with methyl methacrylate, should yield homogeneous, mechanically strong cements composed of acrylic copolymers. Addition of 10 to 15% pentabromophenyl methacrylate to methyl methacrylate yields radiopaque polymers of improved strength. An effort is being made to synthesize iodine containing polymers such as triiodophenyl methacrylate and incorporate them into bone cement formulations.

Future studies are planned to investigate the effects of precoating of metals with polymer, surface activation of curing, surface bonding, preheating of metallic stems and fatigue of new formulations.

Dental and Medical Materials Standards

Subtask 10 of Task 15435

J. A. Tesk, G. M. Brauer, N. W. Rupp, and W. deRijk

Developments of standards for dental and medical materials is strongly supported by activities on committees and subcommittees of ANSI MD 156 (Dental Materials, Instruments and Equipment) and ASTM F-4 (Medical and Surgical Materials and Devices). Leadership roles are held as chairpersons of ANSI MD 156, ASTM F-4, and USA TAG for ISO TC 106, Task group convenor for several working groups of ISO TC 106 and by participation on the Executive Committee of the Medical Device Standards Management Board of ANSI. Numerous standards have been reviewed, edited, revised and reaffirmed for ANSI/ADA and ISO including standards for dental units, chairs, abrasives, burrs and alloys.

DENTAL AND MEDICAL MATERIALS GROUP, John A. Tesk, Group Leader, Task 15435

NBS Personnel

J. M. Antonucci
G. M. Brauer
W. E. Critchley
J. E. McKinney
R. W. Penn
J. W. Stansbury

American Dental Association

R. L. Bowen, Director
W. E. Brown, Dir. Em.
R. L. Blosser
C. M. Carey
M. W. Chalkley
L. C. Chow
W. G. deRijk
N. Eidelman
A. A. Giuseppetti
T. M. Gregory
K. A. Jennings
A. D. Johnson
M. Mathew
D. N. Menis
D. N. Misra
G. C. Paffenbarger
E. F. Prestemon
N. W. Rupp
C. T. Schreiber
L. E. Setz
B. A. Sieck
S. Takagi
B. Tomazic
M. S. Tung
G. L. Vogel
R. M. Waterstrat

Guest Workers

T. S. Chen, FDA
E. Cobb, Georgetown
R. W. Hinman, USN

Industrial Research Associate

S. Venz, Dentsply International

National Institute of Dental Research - Research Associates

E. D. Eanes
B. O. Fowler
A. W. Hailer
H. S. Talwar

G. E. O. Widera, Consultant
with the Univ. of Illinois, Chicago

MECHANICAL PERFORMANCE OF POLYMERS
Task 15436

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 some unique properties of polymers. Important to wider use and acceptance of plastics is a firmer understanding of performance limitations and processes that limit durability. Full utilization of the weight-savings potential of plastics has not been realized due to the lack of adequate data and models upon which to design for long-term use. Evaluation and control during processing of materials parameters that affect performance should lead to more durable materials and reliable performance for the intended service life.

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 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 are: (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 the kinetic theory of bond rupture as a model for degradation of mechanical properties and for extrapolating short-time measurements to predict long-term performance; (3) model failure by neck formation and propagation using time dependent constitutive equations that predict the onset of inhomogeneous deformation from baseline mechanical properties; and (4) expand fracture mechanics approach to viscoelastic materials to model craze and crack growth phenomena.

The National Bureau of Standards has established joint programs on performance of plastics with other government agencies which are fostering the use of plastics in areas of national concern. For example, 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. Elucidation of the molecular and physical structural features that limit the performance of polyethylene film is supported by NASA to improve the success rate of high altitude, heavy lift balloons used in stratospheric research.

Molecular Processes Associated with Mechanical Deformation and Failure
Subtask 1 of Task 15436

B. M. Fanconi, D. L. VanderHart, J. R. Havens, S. J. Kryder and K. L. DeVries[1]

[1]College of Engineering, University of Utah

The identification of those molecular mechanisms and changes in physical structure 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 performance and durability. The characterization of the complex solid state structures exhibited by polymers presents significant challenges. Spectroscopic techniques of ^{13}C and proton nuclear magnetic resonance (NMR) and Fourier transform Infrared (FT-IR) are used to elucidate the physical structure of semicrystalline and amorphous polymers as well as molecular composites. Reorganization of the structure in processing and during use affects mechanical performance. Identification of the molecular events involved and the physical structures that result are the aim of these studies.

FT-IR Studies of Molecular Organization in Polyethylene

Knowledge of the organization of individual polymer molecules in the solid state is prerequisite to elucidation of molecular mechanisms of deformation. Infrared spectroscopy of mixed crystals of polyethylene and perdeuteropolyethylene has been used to provide insights into chain organizations in semicrystalline morphologies. Recent developments in FT-IR spectroscopy that have greatly enhanced the sensitivity of IR and in data analysis procedures, including normal coordinate and IR intensity calculations, have been applied to mixed crystal IR spectroscopy. In this manner, a more refined model of chain organization may be developed. In the initial phase of this project, a method has been designed to calculate the IR spectra of the different arrangements of protonated and deuterated molecular stems on the PE lattice. This calculational procedure has been applied to mixtures of protonated and deuterated n-hexatriacontane and yielded calculated band profiles that were in excellent agreement with the observed IR bands of the CD_2 bending vibration. The calculated IR band shapes were calculated assuming random site selection for the deuterated molecules as the guest in the host protonated n-alkane. Current calculations are aimed at determining the contributions to the calculated IR spectra from sequences of deuterated stems in which random site selection does not hold owing to the long chain nature of polyethylene molecules.

The improved sensitivity of the experimental IR data allowed analysis by the method of self-deconvolution. By this method improved resolution of component IR bands of a complex bandshape is possible by significantly reducing the natural linewidth through calculations procedures. This method has been applied to the CD_2 bending vibration band of a melt crystallized mixed crystal PE sample in which the concentration of the deuterated component was 4% by weight. An intense central peak bracketed by 2 weak bands were resolved from what appeared to be a single band. The central peak was assigned to isolated perdeutero polyethylene stems (no nearest neighbors at nonequivalent lattice sites) and the side bands to pairs of deuterated stems situated on nearest neighbor nonequivalent lattice sites. Through analysis of frequencies and intensities of mixed crystal spectra a more detailed model of molecular organization in the solid state is emerging. Subsequent work will focus on the effects of deformation on molecular organization.

Longitudinal Crystal Moduli of Polymers

In a cooperative effort with Dr. John Rabolt of IBM Research Laboratories the various experimental methods of determining the ultimate longitudinal moduli of polymers were evaluated in light of the wide range of values estimated by these procedures for a given polymer. The ultimate modulus, or longitudinal crystal modulus, is defined as the macroscopic value that would be obtained in a perfectly aligned, fully crystalline polymer. These values serve as bench marks against which progress to produce high modulus materials can be measured. Theoretical values have been derived from calculations of the normal modes of vibration and conformational energy calculations as a function of strain. Experimental estimates are available from x-ray diffraction measurements of the lattice strain of an oriented polymer under applied stress, and from inelastic coherent neutron scattering, Raman spectroscopy, and Brillouin scattering. The last three mentioned techniques are based on observations of the energies and wavevectors associated with longitudinal acoustic phonons. Large and significant discrepancies have been reported between values derived from x-ray diffraction studies and those found by both neutron and Raman scattering.

A composite rod model had been used to explain the up to 5-fold difference between the Raman and x-ray values of longitudinal crystal moduli. This model assumed significant coupling between the longitudinal acoustic modes of the crystalline and amorphous segments in a semicrystalline polymer. In this project, we calculated the effects of such a strong coupling on all longitudinal acoustic modes, rather than just the Raman active modes. This was done for comparisons with the neutron scattering data in which longitudinal acoustic mode frequencies were reported as a function of wavevector over essentially the entire Brillouin zone. From these calculations and the observation that the neutron and Raman techniques yielded virtually the same modulus values for those polymers for which neutron scattering studies have been reported it was concluded that the x-ray determinations of moduli were low owing to the uniform stress approximation needed to extract modulus values from crystal strain data.

Further support for the conclusions reached came from examinations of the effect of temperature on the Raman frequencies of longitudinal acoustic modes. It was found that these vibrational frequencies are virtually insensitive to temperature for melt crystallized specimens whereas macroscopic and x-ray measurements of moduli showed a strong dependence. In addition, macroscopic moduli have been reported that exceeded x-ray estimates of the limiting values. Our findings suggest that the limiting Young's modulus values of polymers are much higher than previously thought, and this observation is important in the quest for high tensile properties polymeric materials.

Chain Scission Mechanisms in Mechanical Degradation of Polystyrene

The role of molecular chain scission in the mechanical degradation of polymers has focussed on fibrous, semicrystalline polymers since chain rupture processes appear to dominate deformation and fracture of such morphologies. Previous work had established that mechanical failure of polyethylene is associated with a critical concentration of chain scissions that accumulated as a result of mechanical stress, deformation and fracture. It was also found that free radicals generated by the initial mechanically induced chain scissions undergo free radical reactions to produce many additional chain scissions before recombining to form stable chemical species. The ratio of bond ruptures to initial free radicals was found to be between 10 and 100 depending on the molecular weight of the virgin polymer and the method of mechanical degradation.

Current efforts have been aimed at establishing the connection between free radicals and bond ruptures in a glassy polymer, polystyrene. For glassy polymers there remains considerable ambiguity about the rôle of chain scission in mechanical degradation as reported using several measurement techniques. The availability of narrow molecular weight fractions for this polymer allowed a realistic comparison of Fourier transform infrared studies of chain scission through detection of new end groups with molecular weight degradation studies using viscometry. Appreciable discrepancies exist between the results of FT-IR and viscometry in the case of polyethylene in which the broad molecular weight distributions may have affected the interpretation of viscometric data.

A systematic study of chain scission in amorphous polystyrene has been conducted using electron spin resonance, FT-IR, and viscometry. The amount of chain scission was determined from the reduction in the viscosity-averaged molecular weights and the increase in molecular end groups. These findings were compared to the number of free radicals generated by mechanical degradation and measured by electron spin resonance (ESR). The degradation was accomplished by grinding the specimens at cryogenic temperatures. Three narrow molecular weight fractions ranging from $2\text{x}10^5$ to $9\text{x}10^5$ were examined.

Infrared difference spectra revealed two bands attributable to new end groups. These bands corresponded to carbonyl vibrations of acetophenone and aldehydic type end groups. The integrated intensities of these bands were converted to concentrations using Beer's law, specimen thicknesses, and absolute extinction coefficients. The last mentioned quantities were taken from literature studies of model compounds. Each new carbonyl group represented one chain rupture process and the numbers ranged from $1.2\text{x}10^{17}$ to $1.33\text{x}10^{17}$ per cc for the three molecular weight fractions. The concentration of chain scissions found from the viscometric measurements was about $1.2\text{x}10^{17}$ per cc while the ESR studies revealed a value of about $0.6\text{x}10^{17}$ per cc. Thus, in contrast to the findings on polyethylene, the FT-IR and viscometric results were in agreement and the extent of the free radical propagation reactions was much less than previously reported for semicrystalline polymers. The insensitivity of the number of chain scissions to molecular weight is related to the low temperature at which degradation was carried out. Low temperatures were used to ensure free radical stability for the course of the ESR measurements. The degradation temperature was below the glass transition temperature and hence molecular mobility did not play a dominant role during deformation. Molecular slippage, involving scission of van der Waals bonds (intermolecular or intersegmental), is a competing process to valence bond rupture. The extent of this process with deformation is greatly reduced at temperatures below the glass transition temperature.

Examination of Drawn PET Fibers by Solid State NMR

This is a continuing joint project with the Firestone Tire and Rubber Company. Motivation is to better understand the molecular organization of these PET fibers so that optimized modulus and shrinkage properties can be engineered into these fibers which are used as tire reinforcement materials.

The current effort was devoted to completing a set of proton NMR experiments, interpreting the results, and writing a paper on this work. The focus of the proton NMR experiments is to use the phenomenon called spin diffusion in order to gain some knowledge about domain sizes of both the crystalline and noncrystalline regions in PET, and to follow their change as a function of processing history. Proton spin diffusion is the transport of magnetization in the presence of a magnetization gradient. The logic of using spin diffusion to study domain sizes in PET is as follows: a) PET consists of heterogeneous regions (e.g. crystalline and noncrystalline), b) heterogeneity of chain packing implies heterogeneity of molecular motion, c) the latter implies differences of relaxation times in the different regions, d) from this follows the tendency for magnetization gradients to develop between regions in a relaxation experiment, and e) since we claim to know the spin diffusion constants quite well, the reduction and disappearance of well-defined gradients generated in this way contains information about domain sizes. The manner of conducting the spin diffusion experiment with least ambiguity is to use multiple-pulse proton NMR to generate the magnetization gradients and to read out the status of the magnetization after some spin diffusion time, given that multiple-pulse proton NMR quenches spin diffusion by removing the dipole-dipole interactions responsible for spin diffusion in the first place.

One of the interesting parameters to come out of the modelling of spin diffusion in the PET fibers was a measurement of the relative change in surface area between the crystalline and noncrystalline regions due to annealing. To our knowledge, this measurement has not been made before. Moreover, at short enough times, this quantity is not dependent on the morphological model used to interpret the spin diffusion data. The results show a decrease in relative surface area of less than 10% for annealing at 200 °C and 30% for annealing at 257 °C relative to the unannealed fiber.

Other results of the analysis show that crystallite thickness changes from 3 to 4 (7) nm as one goes from the original fibers to those annealed at 200 °C (257 °C). Accompanying this is a change in crystallinity from .26 to .34 (.44). Moreover, annealing at 200C with either fixed or free ends seems to result in very similar final domain sizes (however, it is known from the carbon-13 NMR results that the perfection of orientation deteriorates substantially by annealing with free ends). We also were able to differentiate regions of heterogeneous mobility within the noncrystalline regions and were able to show that the coarseness of noncrystalline domain heterogeneity was greater in a drawn sample than in a purely noncrystalline, quenched PET sample. The computer modelling of the spin diffusion data indicated that the long period (the repeating crystalline plus noncrystalline lengths) increases with higher annealing temperatures implying a significant rearrangement of crystalline regions during annealing. Finally, from data obtained on these samples at Firestone, an inverse correlation of crystallite size and breaking strength was noted whereas for those fibers annealed with fixed ends, the modulus at very low strains seemed unaffected by crystal growth. Only at higher strains of 1 to 10% were substantial differences in modulus noted.

Our current experimental work is directed at exploring the nature of the mobility differences observed for the noncrystalline region. We are combining multiple-pulse proton irradiation with proton-carbon-13 cross-polarization in order to investigate whether the differences in noncrystalline mobilities are also correlated with orientation of the noncrystalline chains.

Studies of the Intimacy of Molecular Mixing in High Strength Molecular Composites by Solid State NMR

This is a joint project with the Air Force to explore the potential of NMR for characterization of molecular composites. The Air Force is interested in using polymeric materials as structural materials in airplanes as well as other military goods. They are seeking chemically stable, processable, high temperature, high strength materials. One class of promising polymers consists of highly conjugated aromatic moieties incorporated into the backbone of the polymer structure. Some of these molecules are exceedingly stiff and tend to form rod-like molecules. These polymers are usually difficult to fabricate and must generally be spun out of strongly acid solution. In order to increase the ease of fabrication of these materials and at the same time to take advantage of the inherent reinforcing capabilities of a stiff, rod-like molecule, there has been considerable effort expended by the Air Force to develop high strength composites by blending these rod-like molecules with highly aromatic flexible molecules. The reinforcing efficiency of the rod-like component depends rather crucially on whether the rods aggregate (low strength) or whether they form a molecular composite (high strength). It was this particular question of the intimacy of blending of the two components which we sought to address using multiple-pulse proton NMR. Similar approaches as those used in the PET analysis were envisioned.

Progress has been limited by the lack of suitable quantities of materials containing the right composition for NMR analyses. In addition some specimens contain varying amounts of acids out of which the materials are spun and their presence has hampered the NMR work. Nonetheless some progress has been made as follows:

1. Whereas the proton linewidths of the pure polymers indicate that the polymers are relatively rigid on a time scale of a few microseconds, the composites show excessive motion and it is not clear as yet whether this is the result of the mixing or an artifact from too much residual acid proton signal.

2. In order to detect whether two polymers are intimately mixed, it is obvious that one must be able to determine spectroscopically which signals come from which molecules. In the proton spectra, this is by no means an easy task. Therefore, we have also explored whether a more significant difference can be identified in the carbon-13 spectra. The similarity of the carbon signals between the rods and coils tends to make this approach difficult also.

3. In view of point three above, it seems that one of the most promising materials for NMR investigation is a composite of the aromatic rod-like molecule with a more aliphatic nylon-like coil molecule. In this latter case, carbon-13 resonances arising from each of the components can be singled out using both spinning and non-spinning NMR techniques. A crucial aspect of this problem is whether the proton multiple-pulse techniques can be combined with the cross-polarization method so that proton spin diffusion might be controlled for the investigation of domain sizes. Also the longitudinal relaxation times must be determined to insure that sufficient time is available for spin-diffusion dominated rather than relaxation dominated magnetization changes. The resolution of these questions is part of our future effort.

Intimacy of Molecular Mixing in the Noncrystalline region of a Blend of Isotactic and Atactic Polystyrene Using NMR

Experimental work on a collaborative project with Prof. R. S. Stein at the University of Massachusetts was begun this year. The idea was to investigate compatability of polymers in the glassy state based on differences in tacticity as opposed to differences in chemical structure. We were interested in whether there was any substantial tendency for molecules of differing tacticity to segregate in the solid state. Since we anticipated that the forces for phase separation might be small and that distinctions between packing of nearest neighbors might be quite small, we settled on approaching the question via isotopic enrichment. The NMR tool we employed was proton-carbon-13 cross-polarization (CP). In this method carbon-13 signals are generated by CP from the protons within approximately 0.5 nm from the carbon-13 nuclei. In a blend of protonated and deuterated polystyrenes of differing tacticity one will only be able to cross-polarize the carbons on chains with protonated chains nearby. Since one can also differentiate protonated versus deuterated carbons with the NMR, the experiment is quite straightforward.

Dr. W. Manders of the Center for Fire Research conducted most of the NMR experiments on carbon-13 CP. Starting with fully deuterated atactic polystyrene (PS) and protonated isotactic as well as atactic PS, the relaxation and CP characteristics of six samples (controls and blends) were investigated. Although the results are yet to be fully analyzed, it is safe to say that there is a ranking of the intimacy of mixing as one goes from an atactic/atactic PS glass to an isotactic/atactic glass to an isotactic/atactic partially crystalline sample. Each of these samples was prepared in such a way that the stoichiometry of the two tactic polymers was constant in the disordered phase. Thus it appears that there is indeed a tendency for atactic PS to separate from isotacic PS in the noncrystalline phase. The fact that one still gets a signal from the partially crystalline sample indicates that the domains of phase separation are not large.

We also examined the possibility of determining intimacy of mixing via proton NMR, taking advantage of the fact that the protons in a phase separated, 98% deuterated polymer would generally be rather far from one another so that the characteristics of their signals would change appreciably from those arising from the protonated polymer. This experiment, while excellent in concept, ran afoul of the fact that each of these samples contains some protonated impurities at levels of less than 1% (comparable to the signals expected from the residual protons in the deuterated polymer). In recognition of this impurity, and in recognition of the fact that these impurity protons could, in principle, generate CP signals from the deuterated chain carbons, the role of the proton results became one of proving that the impurity protons were incapable of cross-polarizing the carbons in the deuterated polymer. In this way the CP results were validated as being due to variations in proximity to protonated PS rather than to some impurity.

Orientation Studies on Biaxially Oriented Polyethylene Films by NMR

Recent developments in processing polymers to produce biaxial orientation has led to new products. Such an example is a shotgun shell casing made of biaxially oriented polyethylene. Whereas these cylindrical casings have high strength in the direction tangent to the circular cross-section, they also have significant strength in the direction of the cylinder axis. Only in the direction normal to the film plane does this material show weakness (by delamination). These materials are made by forcing a polyethylene (PE) tube of a smaller diameter over a conical die in a manner similar to the "Bethlehem" process for making materials of similar characteristics. A fundamental question concerning such processes for semicrystalline polymers is the orientation of the noncrystalline component.

We investigated the gun shell casing material with solid state carbon-13 NMR in order to analyze qualitatively for variations in the orientation of the crystalline as well as the noncrystalline material. While x-ray techniques can be used to describe the orientation of the crystalline regions, the NMR technique is more useful for examining the orientational bias within the noncrystalline regions. (The signals from the noncrystalline regions can be separated from those of the crystalline regions because of wide differences in carbon-13 relaxation times.)

The results showed that besides the strong crystalline and noncrystalline orientation expected in the direction tangent to the cylinder cross-section, there was also a bias to both the crystalline and noncrystalline orientation along the cylinder axis as opposed to perpendicular to the film plane. Thus both the crystalline and noncrystalline material showed orientational biases consistent with the mechanical properties.

One other sample was investigated which had been prepared in Prof. Clark's laboratory at the University of Tennessee by another process. This was a film rolled from a thick to a thinner film while keeping the film width relatively constant. The resulting film had single-crystal texture and had similar strength properties as the gun shell casings. The NMR results on this sample were very parallel to those of the gun shell casing.

The Structure and Properties of Low Density Polyethylene Films

Subtask 2 of Task 15436

F. A. Khoury, J. M. Crissman, B. M. Fanconi, H. L. Wagner, L. H. Bolz and C. A Harding

Helium filled 'heavy-lift' balloons, in which the helium is contained by a proprietary low density polyethylene film, are used by the National Aeronautics and Space Administration (NASA) to raise instrument payloads of up to 11500 lbs to elevations of 100,000-150,000 ft. for various research projects. The thickness of the polyethylene film is usually in the range 0.5-1.0 mil. The capacity of the balloons at float altitude can be as large as 50×10^6 cu. ft. Since 1980 NASA has experienced an increased incidence of catastrophic balloon failures during ascent through the troposphere at elevations between 40,000-60,000 ft where the ambient temperature is -70 °C. The causes of the increased failures of this type from 1980 to the present have been elusive.

As part of a broader effort to determine the causes of the balloon failures, a NASA sponsored study has been initiated whose purpose is to examine whether significant differences exist between the proprietary films produced and used in balloons at different times in the last four years as well as prior to 1980. The objective is to establish a basis for determining whether poorer balloon performance in recent years is associated with changes in the mechanical characteristics of the proprietary film due to changes in the raw polymer and/or the bubble process used to produce the blown type of film. Accordingly, an exploratory study has been undertaken to examine various aspects of the structure and mechanical properties of films manufactured at four different periods, including one produced prior to 1980. The following characteristics of the polymer in the various films have been determined: intrinsic viscosity, size exclusion chromatogram (GPC), methyl group content. In addition, the film densities were measured, and differential scanning calorimetry was used to examine the melting characteristics. The film birefringence was also measured, and wide angle x-ray diffraction patterns were obtained for every film with the x-ray beam oriented in three different directions, i.e. normal to the plane of the films, parallel to the machine direction, and parallel to the transverse direction.

Among the differences which have emerged from the experiments listed above is that although GPC indicated that the molecular weight distribution in all the specimens was bimodal, and possibly trimodal, the film produced prior to 1980 had a greater content of higher molecular weight species than the other films. The analysis of methyl group content using Fourier transform infrared spectroscopy indicated that it was ~2·1 methyl groups/100 °C atoms in all the specimens. The weight % crystallinities of the various films, as calculated from the measured densities were very close to one another (46.5%-47.5%), as were the peak melting temperatures (106 °C-107 °C) exhibited in DSC scans at a 20 °C/min. rate of heating.

All the films exhibited negative birefringence with respect to the machine direction i.e. the refractive index parallel to the machine direction was less than that parallel to the transverse direction. The difference in these refractive indices was lowest (-0.0011) in the film produced prior to 1980, and highest (-0.0018) in the film currently used in balloons. The limited x-ray diffraction data obtained so far lend themselves only to qualitative interpretation. It therefore remains to be established, by determining pole figures using a diffractometer equipped with a four circle goniometer, whether the differences in birefringence between the films can be correlated with differences in the orientation characteristics of the crystalline regions in them. The diffraction patterns obtained with the x-ray beam set parallel to three different directions in each film, as well as infrared spectroscopic data, indicate a qualitative similarity in the orientations of the crystalline regions in all the specimens. The distribution of these orientations may well differ between the films. The latter aspect remains to be explored.

Among the aspects of the mechanical properties of the films which were determined and which are of particular interest to NASA is the extension to break, ε(b), exhibited by the films when they are subjected to uniaxial extension in the machine as well as in the transverse direction. All the films exhibited a higher ε(b) parallel to the transverse direction than parallel to the machine direction at 23°C and -70°C, except the film currently used in balloons. In the case of the latter film ε(b) was, on average, almost the same in both directions at room temperature, and was higher in the machine as compared to the transverse direction at -70°C.

It should be noted that the determination of ε(b) in both the machine and transverse directions was carried out on several samples of each film. The averaged measurements for each of the four types of film conformed with the acceptance criterion for use in balloons set by NASA, namely that ε(b) at -70°C should not be less than 250% in both the machine and the transverse directions. The only film in which all the samples tested met this criterion was the one produced before 1980.

It remains to be determined whether the differences in mechanical behavior outlined above can be correlated with specific differences between the structures of the films. In addition to the determination of pole figures, an examination of the fine texture of the films using small angle x-ray scattering is planned. The biaxial deformation (bubble geometry) characteristics of the various films at 23 °C and -70 °C will also be investigated.

The Application of Electron Energy Loss Spectroscopy to Polymers

Subtask 3 of Task 15436

R. M. Briber and F. A. Khoury

The developments in analytical electron microscopy in recent years have resulted in the possibility of obtaining quantitative information on the chemical composition in very small volumes of material. In principle, the composition of regions on the order of a few nanometers in both diameter and thickness can be determined [1]. Among the various analytical electron microscopical techniques available, Electron Energy Loss Spectroscopy (EELS) is a potentially promising one for application to materials, such as synthetic organic polymers, which consist mainly of light elements (atomic number ≦12). The extent to which EELS can be exploited in the study of polymer composition which is of particular interest in investigations of phase separation phenomena in polymer blends, remains to be explored. In addition, the limitations to the application of the technique due to the well known susceptibility of organic polymers to electron beam damage remains to be determined.

The initial goal of this project is to evaluate EELS using polymers of different known compositions in order to assess the influence of such factors as specimen thickness and radiation damage on the quantitative determination of composition, as well as to assess the limits of the spatial resolution which can be achieved with regard to detecting differences in composition in contiguous regions of specimens.

In conventional transmission and scanning transmission electron microscopy a portion of the electrons which pass through a thin sample are scattered inelastically. The energy losses which these electrons undergo are characteristic of the elements comprising the sample and are recorded in EEL spectra as absorption edges which correspond to K and L shell ionizations in the different constituent atoms. EELS has several advantages over energy dispersive x-ray spectroscopy (EDS) for determining the composition of polymers. A major advantage is that the desired signals characteristic of the elements depend on K and L shell ionization cross-sections rather than on fluorescent yield. The former increase, whereas the latter decreases as the atomic number falls. The detection efficiency for light elements is correspondingly enhanced in the case of EELS [2]. The relative amounts of the different atoms present in a sample is obtained by integrating the intensity of the various characteristic absorption edges present in the EEL spectra. It is necessary for this purpose to know the inelastic cross-sections for the various absorption edges corresponding to the different atoms. Furthermore, since the spectrometer detector has a finite angular acceptance and the edge integration is done over a limited energy window, it is necessary to know the partial cross-sections for the particular experimental parameters used. A computer program has been developed by Egerton [3] to calculate the necessary partial cross-sections. Commercially available software systems based on that program have become available for analyzing and interpreting EELS data in terms of sample composition.

Chain-folded polymer crystals grown from dilute solutions are particularly suitable samples to use for evaluating some of the critical parameters (e.g. sample thickness) necessary for obtaining high quality EEL spectra, and for assessing the possible occurrence of changes in composition resulting from beam damage and the formation of volatile by-products containing key identifying elements. One of the basic assumptions in analyzing EEL spectra is that only a single inelastic scattering event has occurred per electron. If the specimen is too thick this assumption no longer holds and quantitative analysis becomes all the more difficult. Accordingly, knowledge of the effect of thickness on the spectral data is an important aspect of EELS. Monolayer polymer crystals are usually on the order of 10nm thick. Crystal preparations usually contain bilayered, trilayered, etc. as well as monolayered crystals, thus providing a convenient set of samples for assessing the effects of thickness on the EEL spectra.

Exploratory experiments have been carried out on crystals of poly(chlorotrifluoroethylene) (PCTFE) which indicate that the optimum thickness for EELS is ~40nm-50nm (3-4 layers). At thicknesses less than that range the signal to noise ratio is low, whereas at higher thicknesses the resolution of the spectra is poorer due to multiple scattering. In these experiments the transmission electron microscopy equipped with an EEL spectrometer was operated in the scanning transmission mode. The electron beam was rastered over an area of the PCTFE crystals of approximately 23μm^2. The scanning rate was such that one complete raster of this area corresponded to one sweep of the spectrometer through the energy loss 0eV-1000eV. Fourteen spectra were successively obtained from the same area. The chlorine to fluorine ratio decreased from about 0.25 for the first spectrum to ~0.05 for the fourteenth. The data extrapolate to a ratio Cl/F about 0.33 at zero electron dose. It was ascertained that the crystallinity of the crystal in the region examined had been destroyed even after the first scan. It is also evident from the EELS data that this is accompanied by a loss of Cl. It is evident from these results that the monitoring of this element to determine the content of PCTFE in polymer blends would lead to erroneous results. Experiments are under way to determine whether exposure to the electron beam also results in a loss of fluorine.

Future experiments will include investigations of the type described above on crystals of several different species of homopolymers (e.g. polyamides, poly(vinylidene fluoride), polyesters) as well as thin films of blends of miscible polymers.

[1] J. J. Hren, J. I. Goldstein, and D. C. Joy, Introduction to Analytical Electron Microscopy, Plenum Press, New York (1979).
[2] M. Isaacson and D. Johnson, Ultramicroscopy 1, 33 (1975).
[3] R. F. Egerton, Ultramicroscopy, 7, 169 (1979).

Handbook on Polymeric Material Used in Orthopedic Devices

Subtask 4 of Task 15436

J. M. Crissman and G. B. McKenna

A materials handbook containing information on the two principal polymeric materials used in orthopedic devices has been prepared for the Food and Drug Administration, Bureau of Medical Devices, as part of task 80-01 NBS-BMD Interagency Agreement. The two materials described are ultra high molecular weight polyethylene (UHMWPE) and polymethylmethacrylate (PMMA) bone cement. UHMWPE is used in the fabrication of implant components such as acetabular cups (hip replacement) and tibial plateaux (knee reconstruction). PMMA bone cement is used to secure the implant components to bone as well as act as a space filler material in the repair of diseased bones. Included in the handbook are sections on specifications (as listed by ASTM), raw materials characterization, fabricated form requirements, processing information, mechanical properties, wear characteristics, and the effects of high energy radiation. The report is intended for distribution to the FDA/BMD staff, resin manufacturers, fabricators, medical researchers, and surgeons.

Mechanical Behavior of Ultra High Molecular Weight Polyethylene

Subtask 5 of Task 15436

J. M. Crissman and L. J. Zapas

Ultra high molecular weight polyethylene (UHMWPE) is used in the manufacture of a variety of orthopedic joint prosthesis. The durability of the UHMWPE component is one factor which limits the time between device implantation and failure. In clinical use, failure of the UHMWPE component has been reported to occur as a result of creep, wear, fatigue associated with wear, and fracture. The mechanical properties, and correspondingly the durability, are determined by the polymer chemistry and morphology related features. Factors such as crystallinity, orientation, spherulite size and texture, as well as molecular weight and molecular weight distribution all influence mechanical performance. Under contract with the Food and Drug Administration, Bureau of Medical Devices, we are now in the final stages of a four year study concerned with the morphology and mechanical properties of UHMWPE. A summary of the earlier work done for this project is contained in previous Polymers Division Annual Reports.

In the 1983 Annual Report the following one-dimensional constitutive equation was presented which describes very well the short time small deformation creep and recovery behavior of UHMWPE in uniaxial extension at 23 °C.

$$\varepsilon(t) = \int_o^t J_*(\sigma(\xi),t-\xi)d\xi + J(\sigma(t),o) + \phi\left(\int_o^t \hat{g}(\sigma(\xi))d\xi\right) \qquad (1)$$

In equation (1), $\varepsilon(t)$ is the strain observed at time t, $\sigma(\xi)$ is the applied stress at time ξ, and $J(\sigma,t)$ is in the manner of a nonlinear compliance multiplied by $\sigma(\xi)$. $J_*(\cdot,\cdot)$ denotes the derivative of $J(\cdot,\cdot)$ with respect to the second argument and $J(o,t)=J_*(o,t)=o$. $\phi(\cdot)$ is a functional which depends on the stress history. The last term represents a plasticity term which describes the nonrecoverable portion of the deformation. It was assumed that in its simplest form the $\phi(\cdot)$ term could be represented by the relation

$$\phi(\hat{g}(\sigma)t) = g(\sigma)t^{\alpha}, \qquad (2)$$

where $g(\sigma)$ is a function of stress alone and σ is a constant. For the case in which the creep and recovery steps are of equal duration it was shown that

$$\Delta\varepsilon_{RC}(t_1;t_1) = g(\sigma)t_1^{\alpha}\,(2-2^{\alpha}), \qquad (3)$$

where $\Delta\varepsilon_{RC}(t_1;t_1)$ represents the departure of the recovery actually observed from that predicted using a superposition principle of the form

$$\varepsilon(t) = \varepsilon_c(\sigma,t+t_1) - \varepsilon_c(\sigma,t). \quad (4)$$

By conducting a series of creep and recovery experiments in which the duration of the creep step was varied from 10^0 to 10^3 seconds it was determined that the UHMWPE at 23°C the exponent α is equal to one third, or

$$\Delta\varepsilon_{RC}(t_1;t_1) = 0.74\ g(\sigma)t_1^{1/3}. \quad (5)$$

It was also found that the creep data would be represented reasonably well by the equation

$$\varepsilon_c(t) = f_1(\sigma) + f_2(\sigma)t^{1/3}. \quad (6)$$

Using this scheme it was possible to describe quite well the creep and recovery behavior (23 °C) of UHMWPE both in single and multistep experiments.

This work has now been extended to include investigation of the long time creep and recovery behavior of UHMWPE and its dependence on temperature. It is found, for example that at times under creep greater than about 10^5 seconds (σ_A=4MP$_a$, T=23 °C) a rather abrupt bend, or break point, occurs in the creep curve beyond which the creep proceeds more slowly and on log-log coordinates the creep curve becomes essentially a straight line. As a result the long time behavior can no longer be described, even approximately, by equation (6). If either the applied stress or the temperature is increased the break point occurs earlier and earlier in time. A similar break point occurs in $\Delta\varepsilon_{RC}(t_1;t_1)$, and for a given stress and temperature occurs at the same time as the break point in the creep curve. For creep times less than that of the break point the exponent α decrease with increased temperature, whereas for creep times longer than that of the breakpoint $\Delta\varepsilon_{RC}(t_1;t_1)$ assumes a constant value nearly independent of temperature. Therefore at long times $\Delta\varepsilon_{RC}(t_1;t_1)$ no longer obeys equation (5). Additional experiments are currrently underway to obtain a more complete description of dependence of both the recoverable and nonrecoverable components of creep on time and temperature.

Investigation of the Strain Energy Function in Model Polybutadiene Networks

Subtask 6 of Task 15436

G. B. McKenna and J. A. Hinkley*

*NASA Langley Research Center, Hampton, VA

The purpose of this research is the study of the phenomenological behavior of model network elastomers. By performing proper mechanical measurements on these model systems it will be possible to provide new information which will help to elucidate the nature of the molecular level events which lead to specific deviations of elastomer behavior from that predicted by the kinetic theories of rubber elasticity.

Considerable effort has been expended in the past to measure the derivatives of the strain energy function using uniaxial extension measurements and to assign specific molecular meaning to the so-called Mooney-Rivlin constants C_1 and C_2. In particular, it has been customary to assign the C_1 term as the modulus value predicted by the kinetic theory and to attribute the C_2 term to such things as chain entanglements, dangling chain ends, etc. The fallacy of this thinking has been pointed out through measurements performed at NBS in the past as well as by other workers in the area of continuum mechanics. The problem arises because the C_1 and C_2 terms arise from the assumption that the derivatives of the strain energy function with respect to the principal stretch invariants, $\partial W/\partial I_1$ and $\partial W/\partial I_2$, of an elastic network are independent of deformation. There is no "a priori" reason for this assumption and, therefore, the representation of $\partial W/\partial I_1$ as C_1 and $\partial W/\partial I_2$ as C_2 and their consequent determination from uniaxial extension measurements cannot provide the appropriate information to researchers doing statistical mechanics of polymer networks in attempts to describe experimentally observed behavior.

In the current research this problem has been addressed by making torsional measurements on model polybutadiene networks. By measuring both torque and normal forces required to produce torsional deformations one can obtain the strain energy function derivatives without recourse to any assumptions about the specific functional form of the strain energy function. No one has actually determined $\partial W/\partial I_1$ and $\partial W/\partial I_2$ for such systems.

We have synthesized two model polybutadiene networks by an endlinking procedure. The molecular weights of the polybutadiene prepolymers were determined from vapor pressure osmometry to be 1.9×10^3 and 3.8×10^3, respectively.

Torsion and normal force measurements have been performed on these networks over a range of strains from 0.006 to 0.50. Preliminary results show that the torsional behavior of both model rubbers is Mooney-like (i.e, $\partial W/I_2=C_1, \partial W/\partial I_2=C_2$) up to approximately $\gamma=0.25$. Beyond this there is a deviation from constant values for $\partial W/\partial I_1$ and $\partial W/\partial I_2$.

Further work to characterize these networks by swelling measurements and determinations of the behavior in simple elongation is currently underway.

Non-Linear Viscoelasticity

Subtask 7 of Task 15436

L. J. Zapas

In the BKZ elastic fluid theory, a knowledge of the single step stress relaxation behavior at various strains is sufficient to describe any other history in strain within the range of strains studied. During the last ten years it has been found that in certain multistep strain experiments the single integral description of the BKZ theory does not quantitatively describe the experiments. A new one dimensional description has been devised which included "cross terms" and which agrees rather well with experiments. If $\sigma(t)$ represents the shear stress at time t and $\gamma(\tau)$ the shearing strain at any time τ then we have the following equation;

$$\sigma(t)=-\int_{-\infty}^{t} H_*(\gamma(t)-\gamma(\tau),t-\tau)d\tau+\int_{-\infty}^{t} F_*(\gamma(t)-\gamma(\tau),t-\tau)\int_{\tau}^{t} \phi(\sigma(\xi))d\xi d\tau \qquad (1)$$

In a single step stress relaxation experiment where the material is at rest for all times τ up to $\tau=0$ and at time $\tau=0$ is strained to a constant value γ, the stress is given by

$$\sigma(t)=H(\gamma,t)-F(\gamma,t)\int_{0}^{t}\phi(\sigma(\xi))d\xi=\sigma(\gamma_1 t) \qquad (2)$$

As is evident the single step behavior given in (2) is not sufficient to describe multistep behavior. By differentiating (2) with respect to t and substituting in equation (1) we get

$$\sigma(t) = \text{BKZ} + \text{terms involving the double integral} \qquad (3)$$

where by BKZ we mean the predictions of the BKZ theory. By assuming that $F(\gamma,t) = K\sigma(\gamma,t)$ we found that $\phi(\sigma(\xi)) = A\sigma(\xi)^2$ gave results in agreement with our experimental data (K and A are constants).

Non-Linear Viscoelasticity of Polymer Solutions

Subtask 8 of Task 15436

L. J. Zapas and G. B. McKenna

In order to test the constitutive equation developed by Zapas (see above) we undertook an experimental program to characterize the nonlinear viscoelastic behavior of a concentrated polymer solution (polyisobutylene in Primol). Single step and multiple step shearing deformations were applied to the solution over a range of deformations from $\gamma=0.5$ to $\gamma\cong25$. Both torque and normal force relaxation responses were recorded continuously at times from 0.5 to 1000 seconds.

There are two results of importance which have developed to date from this study. First, the single step stress relaxation data cannot be described as the product of a function of strain times the shear modulus $(\gamma)*G(t)$ contrary to the theoretical prediction of the Doi-Edwards theory for concentrated solutions and melts. Secondly, the new constitutive equation of Zapas (see above) successfully predicts the shearing behavior of the concentrated PIB solution in multiple step stress relaxation histories.

Superposition of Small Strains on Large Deformations as a Probe of Non-Linear Response in Polymers

Subtask 9 of Task 15436

G. B. McKenna and L. J. Zapas

There are several recent reports [1,2] of using small deformations superimposed on large deformations as a probe of molecular relaxation in polymer glasses. Although the experiments themselves are quite interesting, the use of linear viscoelasticity theory to interpret the incremental response leads to ambiguities, as shown below. There are two important findings which describe the effects of mechanical deformations on the incremental modulus (either $\Delta G(t)$ or $\Delta G^*(\omega)$). First, $\Delta G'(\omega)$ is found to decrease with increasing deformation and to increase with increasing time, t_e, after the imposition of the large deformation [1]. Second, the relaxation spectrum associated with $\Delta G(t)$ is found to increasingly shift to shorter times and to narrow as the deformation increases or as t_e decreases. These results have been interpreted as a form of mechanically induced physical ageing or change in glassy structure [1,2].

The purpose of this work is to show that, although there may be structural changes associated with mechanical deformations of polymer glasses, the superposition of small strains on large strains cannot be treated in the context of linear viscoelasticity. We show this by carrying out experiments on a concentrated solution of polyisobutylene (PIB) in a hydrocarbon oil and on a PMMA glass and rationalize the results in the context of a single integral non-linear constitutive law.

The salient results obtained for the PIB solution are that the incremental modulus, $\Delta G(t)$ in simple shearing histories, decreases with increasing deformation and increases with increasing ageing times. Representation of the incremental modulus as a Williams-Watts function $\Delta G(t) = G_0 \exp[-t/\tau)^\beta]$ shows a shift of the relaxation spectrum to shorter times and a narrowing of the spectrum as deformation increases or t_e decreases. The results are consistent with the concept of additivity of responses in the constitutive equation and are within 15% of the predicted responses at shear deformations as large as 9.5. For the PMMA the effects of the deformation on the incremental modulus are similar to those obtained using the PIB solution, but agreement with the non-linear viscoelasticity theory is not as good. However interpretations of this lack of agreement in terms of change of glassy structure would give the opposite result to that obtained using the linear viscoelasticity theory. These results demonstrate the ambiguity of interpretations of these experiments if one imagines the small strain as simply a linear viscoelastic probe. It strongly suggests that other more direct methods of measurement are called for.

[1] T. L. Smith and T. Ricco, "Physical Aging of a Stretched Polycarbonate Film," paper presented at the 1984 March meeting of the American Society, Detroit, MI.

[2] A. F. Yee, R. J. Bankert, K. L. Ngai, R. W. Rendell and T. K. Lee, "Non-linear Viscoelastic Behavior of Glassy Polymers: Exponential Results and Theoretical Model," paper presented at the 1984 March meeting of the American Physical Society, Detroit, MI.

Measurement of the Time Dependent Strain Potential Function For a Polymeric Glass

Subtask 10 of Task 15436

G. B. McKenna and L. J. Zapas

Several years ago, Penn and Kearsley [1] showed that data obtained from torque and normal force measurements on an elastic cylinder subjected to a twist with the length held constant can be used to determine the derivatives of the elastic strain energy function for an incompressible material. In addition, Rivlin [2] has shown that for single step stress relaxation type deformation histories on viscoelastic materials isochronal data can be treated in the same fashion as equilibrium data for an elastic material. Using these results, we [3,4] subsequently reported, in brief, on relaxation experiments in torsion of poly(methyl methacrylate) in which values of the strain potential function derivatives were obtained assuming that the torsion applied to the material is an isochoric motion, i.e., no volume change occurred. The salient results of this prior work were that $\partial W/\partial I_1$ was found to be negative and to increase (towards zero) with both time and deformation. At the same time $\partial W/\partial I_2$ was positive, greater in magnitude than $\partial W/\partial I_1$, and decreased with both increasing time and deformation.

Although these results were unexpected, they did permit us to explain, qualitatively at least, some unusual results reported first by Sternstein and Ho [5], and observed at somewhat larger deformations by us [4], i.e., the rate of stress relaxation in torsion can be greater than it is in extension, even at relatively small deformations, without invoking a time dependent Poisson's ratio for the material. The reader is referred to reference [3] for a discussion of this.

Although we were able to use our results from the incompressible material analysis quite successfully, we had to acknowledge upon questioning [6] that it was merely an approximation. Furthermore, results obtained by one of us [7] and recent data reported in the literature [8] have shown that torsion of cylinders of polymer glasses results in measurable, albeit small, volume changes.[1] Therefore, we have reanalyzed our results in light of a more exact solution for torsion of a compressible material. We have shown that the compressible material analysis of the torsion problem gave (qualitatively) the same important results as the incompressible material analysis; i.e., that for PMMA $\partial W/\partial I_1$ is negative and $\partial W/\partial I_2$ is positive and greater in magnitude than $\partial W/\partial I_1$.

[1] R. W. Penn and E. A. Kearsley, Trans. Soc. Rheology, 20, 227 (1976).
[2] R. S. Rivlin, Quart. Appl. Math., 14, 83 (1956).
[3] G. B. McKenna and L. J. Zapas, in Rheology, Vol. 3 Applications, ed. by G. Astarita, G. Marucci and L. Nicolais, Plenum Press, New York, 299-307 (1980).
[4] G. B. McKenna and L. J. Zapas, paper presented at the 49th Annual Meeting of the Society of Rheology, Houston, Texas, October 1978.
[5] S. S. Sternstein and T. C. Ho, J. Appl. Phys., 43, 4370 (1972).
[6] J. E. Fitzgerald, Georgia Institute of Technology, personal communication.
[7] G. B. McKenna, R. A. Duckett and A. J. Kovacs, Unpublished data obtained at Centre de Recherches sur les Macromolecules, Strasbourg, France.
[8] T. T. Wang, H. M. Zupko, L. A. Wyndon and S. Matsuoka, Polymer, 23, 1407 (1982).
[9] J. H. Poynting, Proc. Roy. Soc. (London), A86, 534-561 (1912).

---

[1] Interestingly in Poynting's [9] original experiments he was able to measure the dilatation of steel wires subjected to twisting moments. On the other hand Matsuoka [8] and we [7] have found that polymer glasses decrease in volume on twisting whether with free [8] or fixed [7] ends.

The Zero Shear Viscosity of Polystyrene Cyclic Molecules in the Melt
Subtask 11 of Task 15436

G. B. McKenna, G. Hadziiaonnou*, C. Strazielle**, G. Hild**, P. Lutz**, P. Rempp**, and A. J. Kovacs**

*IBM Research Labs, San Jose, CA
**Centre de Recherches sur les Macromolecules, Strasbourg, France

Narrow fractions of polystyrene (PS) molecules in the form of closed, uncatenated rings (cycles) were synthesized by reacting bi-functional "living" precursors with an appropriate coupling agent at very low concentration [1].

Recent theories [2,3] of the flow behaviour of molten polymers model the chain motion by reptation along a curvlinear "tube" formed by the constraints of the surrounding matrix. Since a ring molecule cannot reptate in the conventional sense, its behaviour in shear might be expected to differ appreciably from that of its linear homologue.

In the present work the molecular weight (MW) dependence of the zero shear viscosity (η_o) of melts of cyclic and linear PS fractions is investigated over an $\bar{M}_w$ range encompassing the critical molecular weight ($M_c \cong 40{,}000$) above which entanglements occur in linear PS [4]. Viscosity measurements were performed using a cone and plate viscometer at low shear rates ($10^{-4} < \gamma < 10^{-2}s^{-1}$), and over a wide range of temperatures (120° < T < 210 °C). All the tests were carried out under dry nitrogen to minimize possible oxidative degradation.

The results show that the temperature dependence of η_o of the ring molecules is virtually indistinguishable from that displayed by linear chains, including data obtained earlier by Pierson [5] and Suzuki [6] using the same instrument. The same holds even for molecular weights smaller than M_c for which, obviously, chain ends do not contribute to molecular mobility. One should note, however, that the viscosity of the rings is better described by a power law: $\eta_o \propto \bar{M}_w^{3.6}$, which involves a slightly larger value of the exponent, 3.6 , than the one (~3.4) characterizing linear chains [4-6].

Finally, by assuming two power law dependences for the viscosity-molecular weight relationship it appears that the critical molecular weight, M_c is the same for both the linear and cyclic molecules ($M_c \approx 38{,}000$). The results raise some important questions about the motion of uncatenated rings in a matrix made of similar rings. The unexpected similar behavior of the zero shear viscosity of non-reptating cyclic molecules and that of their presumably reptating linear homologues is surprising. The close similarity in the behaviour of these systems strongly suggests that the contribution of reptation to shear flow may be less important than assumed by recent theories [2,3]. Further work is needed, however, to assess this conclusion.

[1] G. Hild, C. Straxielle and P. Rempp, Eur. Polym. J. 19, 721 (1983).
[2] P. G. DeGennes, J. Chem. Phys. 55, 572 (1971).
[3] M. Doi and S. F. Edwards, J. C. S. Faraday Trans. 2, 74, 1789 (1978).
[4] G. C. Berry and T. G. Fox, Adv. Poly. Sci. 6, 261 (1968).
[5] F. Pierson, Thesis, Fac. Sci. Univ. Strasbourg, 1968.
[6] R. Suzuki, Thesis, Fac. Sci. Univ. Strasbourg, 1970.

Growth Regimes and the Time Development of Lateral Habits in Polyethylene Crystals

Subtask 12 of Task 15436

E. Passaglia and E. A. DiMarzio

It is now well established that polymer crystals can grow in three regimes, generally denoted as I, II and III [1,2]. The most interesting of these regimes for our purposes is regime I. In this case, the growth rate is nucleation controlled. In the idealized case, a nucleus is formed randomly at any point on the growing face and then a strip immediately grows and adds a layer on the face. Thus, the probability of adding a layer to the face is proportional to the length of the face, and non-linear with time is to be expected. In contrast, in regimes II and III, the growth rate is independent of the length of the face.

However, the length of the growing face is lengthened only by growth on faces that intersect it. In particular, in the case of polyethylene, the lateral habit of the crystal is a truncated lozenge formed by intersecting {110} and (200) faces [3]. The {110} faces can only increase in length by growth normal to the (200) faces and conversely. Thus, when at least one of the faces is growing in regime I, the growth rates of the faces are coupled.

This coupled growth problem for the polyethylene case was solved in the following three cases: (1) Both {110} and (200) faces are in regime I, (2) The {110} face is in regime I and the (200) face is in regime II, (3) The {110} face is in regime II and the (200) face is in regime I. The case in which the growth rate of the faces is independent of their length, corresponding to all the other possibilities, has been previously treated (3). In each of the cases, results were obtained for the time development of the crystal dimensions in the a and b crystallographic directions as well as for the aspect ratio, which is the ratio of the length in the b direction to that in the a direction. The results are as follows:

(1) Case 1

(a) After an initial transient, the lengths of the crystal in both the a and b direction increase exponentially with time.

(b) The lozenge shape can never be obtained.

Both these results (but particularly the second) are contrary to experiment.

(2) Case 2

  (a) The length of the crystal in the b direction increases quadratically with time.

  (b) The length of the crystal in the a direction increases linearly with time.

  (c) For long times, the aspect ratio increases with time.

  Growth rates quadratic in time have been observed, but it is possible that the relevant experiments have not been performed. The linear increase of the aspect ratio with time superficially resembles the spherulite case, but in that case the length of the crystal in the a direction probably does not increase with time because of impurity rejection [4].

(3) Case 3

  (a) The length of the crystal in the b direction increases linearly with time.

  (b) After an exponential transient, the length of the crystal in the a direction also increases linearly with time.

  (c) For long times, the aspect ratio is always that of the lozenge.

All these results follow directly from the regime I requirements that nucleation occurs sporadically on the growing face and that rapid growth occurs subsequently. Although the critical (but difficult) growth rate experiments at constant concentration have not been performed, these results are contrary to the experiments that have been done. Hence the conclusion is that the regime I requirement does not obtain. This can come about by having the growth face broken up into a number of small, independent facets, or by having nucleation occur preferentially at the corners of the crystal.

[1] J. D. Hoffman, G. T. Davis and J. L. Lauritzen, Jr. in Treatise on Solid State Chemistry, (Ed. N. B. Hannay), Plenum Press, N.Y. 1976, Chap. 7.
[2] J. D. Hoffman, Polymer 24, 3 (1983).
[3] E. Passaglia and F. Khoury, Polymers 25, 631 (1984).
[4] H. D. Keith and F. J. Padden, J. Appl. Phys. 35, 1270 (1964).

Determination of Defect Structure from Infrared Spectroscopy
Subtask 13 of Task 15436

D. H. Reneker and J. Mazur

Conformational defects which allow polymer chains to move through polymer crystals can affect the mechanical and other physical properties of polymers such as polyethylene. In this work infrared spectroscopy is investigated as a tool for observing and characterizing conformational defects in polyethylene.

A computer program was developed to calculate the vibrational intensities in a n-alkane crystal containing a defect. This program determines an intensity vector associated with each methylene group in the molecule, in addition to the total infrared intensity associated with each eigenfrequency. The method is based on normal coordinate calculations and a given set of electro-optical parameters for n-alkanes. Comparison with the infrared spectrum of n-alkanes and crystalline polyethylene shows absorption bands not associated with a regular, zigzag-like structure of a molecular chain in a single crystallite of polyethylene.

Computer graphics are employed to display molecular structure, displacements and dipole moment vectors associated with the CH_2 groups. Stereographic views are used to show how the defect contributes to the infrared intensity associated with modes not present in perfectly crystalline material. The calculations and computer graphics reveal the conformations which contribute to each absorption band.

PROCESSING AND RELIABILITY OF POLYMER COMPOSITES
Task 15437

The great emphasis on light-weight, energy-efficient structures is producing a rapid growth of composite materials as a high payoff application of polymers. The addition of a reinforcement, either particles or fibers, to polymers can dramatically improve their performance, and as a result they can be utilized in a wide range of generic applications where the requirements are beyond the capabilities of simple polymers. This expanded potential has led to increased usage in diverse areas ranging from transportation to construction. In addition to their light-weight, major factors behind the expanded applications of composites include versatility in fabrication, high corrosion and fatigue resistance, and the potential to significantly reduce the need for critical materials such as cobalt and chromium whose limited supply is of critical concern to the national interest.

Although composite materials have great potential, the same multicomponent composition that is responsible for their high performance also gives rise to numerous problems with regard to processing and reliability. Since the composite field is still at an early stage of development, many of these problems can be directly attributed to a lack of basic knowledge and adequate test methods. This task represents a response to that need. The objectives in this Task are to carry out long range research to provide industry and other Government agencies with test methods, materials property data and failure prediction models that are essential if the full potential of these materials is to be achieved. The Task involves two major thrusts that are associated with the major problem areas in the composites field: processing and reliability. The first thrust seeks to gain a better understanding of the basic science involved in processing and fabrication of these materials while the second addresses the development of the fundamental science concepts, methods, and data needed to assist in improving durability and enhancing the capability for failure predictions.

Task programs have been developed to address both areas of concern. A number of projects are studying cure, i.e., the chemical reactions that occur during processing and represent the most important factor in successful fabrication. The work combines a variety of nondestructive measurement techniques so that a thorough understanding of the processes involved can be developed. The potential for employing one or more of these techniques for real time on-line control of cure is also being addressed. The second major thrust area concerns the failure behavior of both particle and fiber reinforced polymers. Special emphasis is placed on the development of techniques, such as neutron scattering, which can provide information about the state of the material before and during failure. The programs seek to understand the basic failure mechanisms in polymers and how these mechanisms are transferred into composites.

To assist in conducting this broadly based effort, the task is utilizing a number of cooperative programs as well as the services of experts who spent time working in the Division during the last year. The cooperative efforts involve programs with NASA Langley Research Center, the Department of the Treasury, and the industrial research laboratories at Hercules and Hexcel. In addition, a number of guest workers and visiting scientists have greatly contributed to the programs during the past year. These include Dr. Alan Gent from Akron University, Dr. S. S. Wang from the University of Illinois, Dr. J. T. Koberstein and Mr. J. N. Owens from Princeton University, and Mr. A. Gilat and Mrs. H. Weisshaus from Israel. Finally, cooperative research efforts are continuing with Dr. A. J. Kinlock in England and Dr. H. Benoit in France.

Cure Kinetics Measurements on Polymer Composite Matrix Materials and Crosslinking Systems

Subtask 1 of Task 15437

G. A. Senich, J. C. Phillips, H. Weisshaus, and J. H. Flynn

Increasing concern over energy efficiency is placing greater emphasis on the development of light-weight structural components in transportation, construction and other energy-intensive applications. Polymer composites offer a great deal of promise in this area. The multicomponent nature of these materials, however, can lead to problems during processing such as nonuniformity or part to part variability in performance. Better characterization of the kinetics of the curing that occurs during processing can provide important information needed for successful fabrication. In addition, tests of this type can also be valuable for evaluating the effectiveness of various other crosslinking systems such as components in composite thin films, coatings, and inks.

Several nondestructive measurement techniques are being used during cure of identical samples for analysis of the reaction kinetics of crosslinking systems. Polymerization of the thermosetting systems of interest, epoxies and acrylated and unsaturated oligomers, is being initiated with ultraviolet radiation or by thermal means. Fourier transform infrared spectroscopy (FTIR) is used to determine the extent and rate of reaction for the participating chemical functional groups. Differential scanning calorimetry (DSC) is used to monitor thermally the kinetics of these exothermic cure processes. Steady state viscosity determinations give a physical property indication of the overall speed of cure while ultrasonic shear wave experiments provide information on the change in mechanical properties occurring. By comparing and correlating results for the same material, it is possible to obtain a more thorough understanding of the kinetics of the cure chemistry occurring during processing of thermoset materials.

For an uncured resin with acrylate groups, a typical infrared spectrum has prominent carbon-carbon double bond stretching features from 1660 to 1615 cm^{-1}. Upon photocuring or thermal curing, a major reduction in absorption for the stretching bands which undergo polymerization is observed along with significant changes in the fingerprint region. Examination of differences in FTIR spectra can further elaborate on the chemical structures involved. A series of spectra obtained by subtracting the infrared absorbance of a sample cured for varying amounts of time from that for the uncured sample has both positive and negative absorbances. The positive absorbances indicate species present in excess in the uncured material, such as unreacted carbon-carbon double bonds, while negative absorbances arise from species present in excess in the cured resin, such as new crosslinks formed during cure. The progressive decrease in double bond concentration with longer cure time is readily apparent as a change in magnitude of the carbon-carbon double bond stretch absorbance maxima. This information serves as a basis for quantitative evaluations of the change in concentration of reacting functional groups occurring over time during cure.

The polymer systems of interest for composite matrices undergo polymerizations which are usually quite exothermic. Consequently, DSC is a natural method for investigating cure kinetics of these materials. The rate of the polymerization is obtained directly from the amplitude trace of the DSC. Since a single polymerization mechanism is often operative throughout most stages of the reaction, the area under the DSC trace is equal to the enthalpy of polymerization and the extent of chemical reaction will be linear with enthalpy production. This is often not the case when mechanical or other properties of the system are used to monitor polymerization kinetics. The DSC amplitude trace during thermal curing rapidly reaches a maximum value after initiation and then falls off monotonically with time. Measurements of the extent of reaction indicate that the "tail" of these curves may contribute 10-20% to the total polymerization process; this latter portion of the reaction is necessary for attaining the desired final physical and mechanical properties of the cured resin. The rate of polymerization decreases with time according to second order kinetics. It is important to know whether the decay of the DSC curves is limited by the reaction enthalpy change or by the low thermal conductivity of the specimens. Therefore, thermal resistance has been measured for cured polymer discs. The results indicate that specific rates are limited by the enthalpy production of the cure reaction of interest and not by heat flow.

Monitoring the viscosity of a curing thermoset material under steady shear allows evaluation of effects of temperature, concentration, and shear rate on the rate of cure. The rate of change in viscosity with time, the time delay before the effect of curing on viscosity is measurable, and the time required to reach a given viscosity all give information on the kinetics of the polymerization process [1]. The chemical reaction rate constant can be determined from the rate of change of viscosity with time if the viscosity behavior is found to obey the predictions of models for the curing process, while activation energies for curing are determined from the temperature dependence of either these rates or of cure time data. The effect of increasing the initiator concentration is readily evident as an increased rate of viscosity change with time and a corresponding reduction in the time to the onset of cure.

Ultrasonic analysis is mechanically sensitive to the liquid to solid transformation which occurs when thermosets cure. A quartz substrate coated with the curing sample is subjected to shear deformations in the ultrasonic frequency range. A shear deformation is employed because of the extreme differences in shear properties of liquids and solids. Ultrasonic frequencies are used because the high attenuation of shear waves in polymers over this frequency range allows a film to be treated as if it were infinitely thick, simplifying mathematical analysis. It is impossible to observe the shear wave generated in the polymeric sample, but shear wave changes in the quartz substrate are readily apparent. By analyzing the wave in the strip before and after the sample is applied and throughout the cure, the shear storage and loss moduli of the crosslinking polymer can be determined from changes in the velocity and attenuation.

However, qualitative evaluation of mechanical properties is often sufficient for characterizing cure and this information is obtained for the systems of interest by monitoring attenuation only.

[1] G. A. Senich, W. J. MacKnight, and N. S. Schneider, Polymer Eng. Sci. 19, 313 (1979).

In-situ Characterization of the Interface Regions of Glass Reinforced Composites

Subtask 2 of Task 15437

F. W. Wang, R. E. Lowry and B. M. Fanconi

Polymer matrix composites are desirable materials owing to their high specific strength and modulus and corrosion resistance. Wider application of these materials is limited by product variability and the labor intensive, time consuming manufacturing processes. Recent advances in automated, computer controlled manufacture have been encouraging, although limited by the lack of suitable process monitoring. The manufacture of polymer matrix composite materials involves complex chemical and physical processes that must be adequately controlled to produce desirable products. Lack of adequate control during processing may result in poor quality and high rejection ratios in large volume productions. Monitoring techniques and models to correlate monitoring data to improved processing are key aspects to increasing production rates and product quality.

The major chemical change that occurs in processing is the transformation from liquid monomer, or prepolymer, to the solid, cross-linked polymer matrix. Chemical reactions that bring about this transformation are influenced by temperature, pressure, type and concentrations of inhibitors, accelerators, and monomers or prepolymers, as well as the chemical nature of coupling agents on the reinforcement fibers. In addition, molecular mobility, viscosity, and the glass transition temperature will affect the extent of the cross-linking chemical reactions (degree of cure) that form the three-dimensional structure of the matrix. The chemical and physical structure at the polymer matrix-reinforcement interface is thought to have a significant effect on properties and performance. As the interfacial region encompasses an exceedingly small volume of material that is difficult to probe, there has been a dearth of knowledge about this important region. De-bonding at the interface can adversely affect mechanical properties of composites, and as this failure mode is influenced by the chemical and physical structure of the matrix polymer at the interface, methods of probing the interface region during processing may impact significantly the durability problem.

Control of resin viscosity during processing through temperature and pressure is the fundamental aspect of quality manufacturing, and this project addresses the need for in situ monitoring of viscosity. The approach is based on fluorescence spectroscopy and the sensitivity of some fluorescent dyes to the microviscosity. The state of the probe dye molecules is interrogated by laser light brought into the specimen by optical fibers. These fibers may be part of the reinforcement network of the composite under inspection.

In the initial phase of this project optical waveguide measurement systems have been designed and preliminary investigations for design optimization have been completed. Our preliminary measurements have also demonstrated that, under some favorable conditions, the fluorescent light of a compound in the interfacial region around an optical fiber will enter the fiber and emerge, together with the exciting light, at the end of the fiber. We have found that the spectrum of this fluorescence can be measured after the removal of the exciting light with a filter. These preliminary measurements were carried out on a system in which the 496.5 nm light from an argon-ion laser propagated in a glass fiber immersed in a mixed solvent of o-dichlorobenzene and n-propanol containing the dye rhodamine B. We are now investigating a similar system in which the glass fiber is embedded in an epoxy resin containing rhodamine B. It appears that the index of refraction difference between the fiber and the matrix is a key aspect in determining the amount of fluorescent light captured by the fiber. Experiments are underway to establish the optimal conditions for fluorescence detection.

We have also applied the excimer fluorescence technique to monitor the viscosity change during the cure of an epoxy resin. A trace amount of 1,3-bis-(1-pyrene)propane was dissolved in a stoichiometric mixture of Epon 828 (diglycidyl ether of Bisphenol A) and methylene-bis-(cyclohexylamine). The intensity ratio F_M/F_D, where F_M and F_D are the fluorescence intensities of the pyrene fluorescence and the pyrene-excimer fluorescence, was measured as a function of time after the mixture was heated to 60°C. The measured values of the intensity ratio successfully indicated the initial decrease of the resin viscosity due to heating and exothermic reactions, and the subsequent increase of the resin viscosity due to polymerization reactions.

Another aspect of the project concerns the selection of suitable dyes whose fluorescence properties are more sensitive than that of 1,3-bis-(1-pyrene)propane to the viscosity change in the later stage of the resin curing. Michler's ketone, aurin, and basic Fuchsin were found to be suitable as viscosity probes, since their fluorescence intensities increase several-fold during the cure of an epoxy resin.

Cure Monitoring in Polymers and Composites via Dielectric Spectroscopy
Subtask 3 of Task 15437

F. I. Mopsik

The rapidly expanding use of polymers in structural applications has generated much interest in the new field of polymer processing with chemically reacting (i.e., polymerizing) materials. Unfortunately, there is a general lack of knowledge concerning how to control the processing of such systems. This has produced an urgent need to investigate the basic science of processing with reacting polymers and to develop nondestructive test methods for process monitoring. One particularly promising test method is the use of dielectric measurements. This technique has both the advantage of being nondestructive and the potential for on-line application leading to process control.

The measurement of dielectric properties can provide information on molecular mobilities that is quite valuable for process monitoring. This information is especially useful if one can measure dielectric properties over a wide range of frequencies so that a good picture of the molecular relaxations can be obtained. With the conventional approach to dielectric measurement, however, this is not possible for systems such as curing polymers that change rapidly. The newly developed NBS Time Domain Dielectric Spectrometer (Ref. 1) provides a unique capability to overcome this problem through its high measurement speed.

During the last year an effort has been made to implement this technique and these studies have revealed two problem areas that were overcome. First, although the measurements are nondestructive, curing involves irreversible reactions that cause the resin to adhere tightly to the electrodes making them unsuitable for reuse. Consequently, inexpensive (i.e. disposable), three-terminal measurement electrodes based on printed circuit board technology were designed and fabricated. This system allows accurate measurements to be made with a reproducible geometry, thus facilitating standardization of the measurement.

The second problem area involves the high conductivity of the polymer resins prior to gelation. This high conductivity overshadows the dielectric measurement in the early phases of cure. To address this difficulty, a real-time, automated AC conductivity measurement system has been developed. This will permit the monitoring of the early phases of curing by following conductivity changes at low audio frequencies. In addition, the data obtained will help establish at what point in the cure the more complex (but more informative) time-domain measurement can be used effectively. It is expected that only after the resin has begun to gel will dipolar loss mechanisms begin to become dominate over ionic conductivity. By combining both measurement techniques, the entire cure process can be monitored.

Initial experiments with this new two measurement system have been conducted and the results are very encouraging. Further development of the method using model resin systems is planned for the coming year.

1. F. I. Mopsik, "Precision Time-Domain Dielectric Spectrometer", Rev. Sci. Instrum. 55, 79 (1984).

Quality Control Tools for the Processing of Cross-linking Polymer Systems

Subtask 4 of Task 15437

G. W. Bullman, E. A. Debelius and D. L. Hunston

Cross-linking polymers represent a general class of commerically important materials that are used in a wide range of applications including composites, adhesives, paints, coatings and inks. The performance of such materials depends on the proper progression of the curing reactions during fabrication. Unfortunately, a great many factors influence these reactions, and thus the control of cure chemistry is a difficult problem. One important aspect of the solution to this problem is quality control of the starting materials. In some cases chemical analysis represents the best answer, but there are examples where the formulations are so complex that chemical analysis is difficult and not necessarily completely satisfactory. One example of this situation is the area of complex printing inks. In response to a request from the Bureau of Engraving and Printing, we have been conducting experiments to develop new quality control tools for selected ink formulations. After much study, it was found that the most reliable quality control tests involve the use of cure monitoring techniques which can be used to evaluate the cure rates for small ink samples from each ink batch. Experiments using a variety of cure monitoring methods show that substantial batch-to-batch variations in cure rate are present and can be detected. When the cure rate was within a given range, the ink performance was generally good, but when the rate was outside that range, poor ink performance often resulted.

Characterization of Epoxies by Neutron Scattering

Subtask 5 of Task 15437

W. L. Wu and B. J. Bauer

Thermoset polymers have been used extensively as the matrix resin for composites. The properties of these thermoset polymers play a critical role in determining certain essential properties such as the damage tolerance and the toughness of the resultant composites. The polymers involved are amorphous glasses comprised of crosslinked molecular networks. A technique is urgently needed for characterizing the network structure of these polymers in terms of the homogeneity of the crosslinks and the response of these crosslinks under stress. With this structural characterization technique available, the relationship among the compositions, processing condition and the performance of the matrix materials can then be established systematically. The use of coherent elastic neutron scattering provides an exciting opportunity for addressing this problem.

The feasibility of such an approach has been demonstrated recently with model thermoset systems. A partially deuterated epoxy, the diglycidyl ether of Bisphenol A (DGEBA), was synthesized. Perdeuterated phenol and acetone were condensed to give perdeuterated Bisphenol A. It was then reacted with epichlorohydrin to give an epoxy with 14 deuterium atoms in a central position. The network was formed by reacting the DGEBA with di or triamines based on polypropylene oxide flexible chains.

The scattering was performed on the small angle facility and with a BT-6 diffractometer. Multiple scattering peaks were observed in these amorphous materials, and intranetwork correlation among the deuterated segments was associated with these peaks. The homogeneity of the network structure could be successfully characterized with a paracrystalline model and the results suggest that the molecular structure in epoxies is far from the ideal homogenous network.

Matrix Resin Effects in Composite Delamination: Mode-I Fracture Aspects

Subtask 6 of Task 15437

D. L. Hunston, W. D. Bascom,[1] R. J. Moulton,[2] and N. J. Johnston[3]

[1]Hercules, Graphite Fiber Aerospace Division, Magna, UT
[2]Hexcel Aerospace Corp., Dublin, CA
[3]NASA Langley Res. Cen., Hampton, VA

The design of optimized composite materials is characterized by the need to make complex trade-offs among a variety of strongly interrelated properties. At present this is a highly inexact process because these interrelations are seldom known or understood in any detail. As a step toward a more scientific approach to composite materials development, it is useful to investigate the relationship between the properties of the composite itself and the behavior of its constituents. One area of particular concern is composite delamination. The purpose of this work is to investigate the role of the matrix resin in determining the resistance of a composite to the growth of interlaminar cracks. The results to date focuses on one aspect of the problem: the relationship between the mode-I fracture energy of the matrix material in bulk samples and the fracture energy for mode-I like interlaminar crack growth as measured by the double cantilever beam specimen.

A wide variety of thermoset, toughened-thermoset, and thermoplastic polymers have been examined in both test geometries. The results show a clear correlation between the data from the two types of experiments. With brittle polymers (fracture energy less than about 200 J/m^2) the composite fracture energy is, on average, about 2.3 times that for the resin. The additional toughness in the composite has been attributed to fiber breakage and pull out during crack growth. For matrix resins with higher toughness, a trend of about 3.2 to 1 is observed; i.e., on average an increase of 3.2 J/m^2 in the resin fracture energy results in approximately a 1 J/m^2 increase for the composite. This less than complete transfer of toughness has been attributed to the fact that the fibers: (1) restrict the crack-tip deformation zone in the polymer, (2) change the details of the crack tip stress/strain field, and/or (3) physically reduce the amount of resin in the deformation zone by occupying some of the space. These arguments are supported by the observation that the transition between the two types of behavior occurs at a point (~200 J/m^2) where the size of the deformation zone is roughly comparable with the fiber-fiber spacing between plies.

The experiments also demonstrate factors other than matrix toughness that influenced interlaminar fracture energy. Factors that tended to increase the resistance to interlaminar crack growth are fiber nesting and bridging while factors that tended to decrease this resistance include weak fiber-matrix bonding. This latter factor was found to be particularly common in the thermoplastic composites. They generally exhibited lower interlaminar fracture energy than the corresponding thermoset composites and scanning electron microscope pictures of the fracture surfaces in the thermoplastic composites showed extensive interfacial failure.

New Test Methods for Composite Delamination
Subtask 7 of Task 15437

D. L. Hunston, G. W. Bullman, W. D. Bascom,[1] and A. Gilat[2]

[1] Hercules, Inc. Graphite Fiber Aerospace Division, Magna, UT
[2] Armament Development Authority, Haifa, Israel

A major failure mechanism in fiber-reinforced composite materials is delamination, i.e., the growth of cracks between the fibers in the polymer that holds the composite together. To study this type of failure, however, there is a need to develop new test methods and/or perfect existing techniques that assess the resistance of the composite to this type of crack growth. During the past year, our efforts have focused on the double cantilever beam test geometry and a modified version of this specimen in which the sample is tapered to simplify the data evaluation. These studies have examined a wide variety of specimen sizes and shapes and compared the data with the results for the commonly used double cantilever beam (DCB) geometry. The experiments have included composites made with 4, 12, 24, 48 and 64 layers of fibers. The effects of various patterns of fiber directions were also studied. The results (1) indicate that the tapered specimen was simpler to use and gave results equivalent to those obtained with conventional DCB specimens. On the other hands, the experimental scatter was somewhat larger than that found for the more time consuming DCB procedure. As a result, it was concluded that the tapered specimen is most useful for quality control experiments where the gain in simplicity compensates for the small loss of precision.

(1) W. D. Bascom, G. W. Bullman, D. L. Hunston, and R. M. Jensen, Proc. SAMPE National Meeting, Reno, April, 1984.

Detection of Delamination in Fiber Reinforced Composites
Subtask 8 of Task 15437

W. Wu

Delamination is one of the dominant failure modes in many fiber reinforced composites. Techniques for quantitatively characterizing the delamination process are needed to provide the basic information regarding the initiation and growth of delamination cracks.

Small angle neutron scattering (SANS) was found to be a useful technique; the scattering background due to the fiber-matrix interference can be minimized rather easily by matching the scattering length of the fiber and the matrix materials.

Experiments using SANS to monitor the delamination process in KEVLAR-POLYIMIDE composites (0°/90°) were undertaken, and the results fully demonstrated the viability of the SANS technique for this purpose. In the early phase of the delamination process, the formation of a microcrack layer surrounding the fibers is the major event. The later stage of the delamination process is the coalescence of these microcracks to form cracks. The SANS technique will be used in the future to investigate delamination and similar damage processes.

Interfacial Bonding in Composite Materials
Subtask 9 of Task 15437

R. E. Dehl, S. S. Chang, and J. R. Maurey

Composite materials are being developed which have mechanical, thermal, and corrosion properties superior to those of traditional single-component polymers, metals, or ceramics. In many applications, the cost and weight of the materials involved as well as their performance have been substantially improved by the substitution of composites for the original one-component materials. A major requirement in insuring the stability and durability of any composite, however, is the ability to bond together two or more constituent materials that make up the composite. This problem is especially difficult because the components of a composite are almost always quite different in chemical and physical properties. The interfacial bonding is crucial because a major failure mechanism is the growth of cracks between the fiber or particle reinforcement and the matrix resin, usually a thermosetting polymer, that holds the material together. This failure mechanism is an important problem in applications as diverse as aerospace vehicles, dental and medical prostheses, and encapsulants for fragile devices such as microelectronic circuits.

It is known that the bonding of dissimilar materials can be enhanced by the application of coupling agents to the interfacial surfaces because these agents form a strong and resilient bridge between the two phases. In an attempt to gain a better understanding of interfacial bonding, we have undertaken a systematic study of the effect of coupling agents on the adhesive stength of a model system consisting of glass microscope slides bonded with epoxy resins. The strength of the interfacial bond is tested by inserting a wedge between the slides and observing whether eventual failure occurs adhesively at the interface or cohesively in the glass or the epoxy matrix. If failure does not occur at the interface, the bonded slides are subjected to hydrolysis or other solvent treatment at elevated temperature for periods of one hour or more, and retested for interfacial bond strength. We are measuring the strength of the glass-epoxy bond as it is influenced by the chemical nature of the bonding agent, the thickness of the coupling agent film, the chemicals used as initiators and cross-linking agents in the resin, and particle fillers in the resin. These studies are providing valuable insights into the nature of interfacial bonding in such systems. The ultimate goal is to identify and optimize those factors that produce strong and resilient interfacial bonds in composite materials.

Viscoelastic Properties and Fracture of Polymers
Subtask 10 of Task 15437

D. L. Hunston, G. W. Bullman, A. N. Gent,[1] and A. J. Kinlock[2]

[1] The University of Akron, Dean of Graduate Studies and Research, Akron, Ohio

[2] Ministry of Defense, RARDE, Waltham Abbey, Essex, England

Many of the polymers that are used in composite materials exhibit viscoelastic behavior. If the properties and failure behavior of these composites are to be understood, the viscoelastic behavior of the polymers involved must be studied. To address this problem, a variety of model systems are being examined. One such system is a plasticized polyvinyl chloride. When reinforced, this material is of interest to the Navy for certain compliant coating applications. For studies of viscoelasticity, this material has the advantage that its glass transition is near room temperature, and as a result properties like fracture can be investigated throughout the entire transition region. Experiments are currently underway to measure both the basic viscoelastic properties and the tear strength for various formulations of this material.

Two other model systems are also being studied. Both are particle reinforced composites: a polytetrafluoroethylene filled polysulfone that is used by the Navy in seal applications and a rubber-modified epoxy that models the behavior of structural adhesives. In the latter case, the failure behavior was measured as a function of temperature and loading rate over a wide range of test conditions. The fracture energy for the initiation of rapid crack growth varied by almost 2 orders of magnitude but these variations can be rationalized based on a crack blunting argument (1,2). When the temperature is increased or the loading rate is decreased, there is more crack-tip yielding, and this produces increased blunting. Such blunting decreases the local stress concentration at the crack-tip thus permitting larger loads to be reached before rapid crack growth initiates. As the blunting increases, the crack growth becomes unstable. This can be understood by noting that once the crack starts to move there is less time for the material to yield at the crack tip, and thus the crack gets sharper. This increases the local stress concentration effect, and so long as the drop in load is not too rapid, unstable situation is produced.

The crack-tip radius corresponding to the different degrees of crack blunting produced by the various test conditions can be estimated with simple models. To demonstrate that there is a unique correspondence between this radius and the fracture energy, samples were prepared with known crack-tip radii and tested to failure (1,2). The fracture energies for these specimens were identical to those where the same radii were obtained via natural blunting. A simple failure theory (1,2) was developed based on the criteria that failure occurs when a critical stress level is reached at a critical distance ahead of the crack-tip. This model successfully predicts the failure for both those samples where natural blunting occurred and those where the crack-tip radius was artifically generated. This model not only helps to explain the results but also provides a unique failure criteria for these polymer systems.

(1) A. J. Kinloch, S. J. Shaw, D. A. Tod, and D. L. Hunston, Polymer, 24, 1341 (1983).
(2) A. J. Kinloch, S. J. Shaw, and D. L. Hunston, Polymer, 24, 1355 (1983).

Effect of Fillers on the Swelling Ratio in Composites

Subtask 11 of Task 15437

W. L. Wu

It is well known that the equilibrium swelling ratio of the resin within a composite is less than that of the same materials in its neat form. The extent of the suppression in the resin swelling ratio has also been found to be dependent on the filler content. The basic reason for the above observations is that the resin at the filler-resin interfaces loses a certain amount of freedom for expansion.

A quantitative account for the above reasoning has been advanced for both the fiber and the particulate reinforced composites. Analytic solutions for both types of composites in *theta* solvents has been obtained. As to other solvents, the deviations in the swelling behavior from that of the *theta* solvents is predicted to be merely a function of $n\ (1-2X)$; where n is the molecular weight between crosslinking points within the resins and x is the solvent resin interaction parameter. Numerical solutions for the non-theta solvents cases have also been obtained by solving a second order nonlinear differential equation.

The experimental data from our laboratory and others confirm the above prediction.

MICROSTRUCTURE AND PERFORMANCE OF DIELECTRIC PLASTICS
Task 15439

The goal of the task on electrical properties is to carry out long range research to provide the basis for new or improved measurements and provide concepts and data which will lead to higher performance in the electrical applications of polymers. The research encompasses a broad range from insulating materials with low loss to materials that conduct either electrons or ions. An important part of the program includes research on polymers that can be made to exhibit piezoelectric and pyroelectric properties which has led to new types of transducers and new measurement capabilities. Results of the research in the form of data, measurement techniques, and scientific concepts go directly to funding organizations through written reports or in some cases by the delivery of a measurement system. The information is made available to interested parties in the general public by publication in archival journals, by presentation at the meetings of technical societies, through research associates who come to work with us, and by visits to our laboratories.

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 and to determine the regions of frequency and temperature where they can be expected to perform best as insulators. Development of a time-domain dielectric spectrometer at NBS has extended the utility of these measurements to follow dielectric properties which evolve as a function of time since data for a wide range of frequency can be obtained in a time interval comparable to the reciprocal of the minimum frequency of interest. Dielectric measurements are being explored as a means of following the cure of epoxy resins and the change in polymer properties under use conditions. Our competence in dielectrics is also being applied to the development of a stable, reproducible system to simulate the dielectric properties of human tissue to be used in hyperthermia studies in cancer research.

Polymers have long performed well as insulators but higher demands are now being made on their electric breakdown strength as the electric power companies increase voltage of power transmission. Longer lifetimes in more hostile environments are required as the trend to underground cables continues. A more fundamental understanding of electrical breakdown is required to address these problems. A thermal pulse measurement technique which has proven useful for determining distribution of polarization in polymer films offers an opportunity to measure the distribution of charge in insulation film and thus study the role of non-uniform electric fields in determining the breakdown strength in polymers.

NBS has made a significant contribution to the understanding of the mechanism responsible for the piezoelectric and pyroelectric properties of polymers. There is a need for predicting their long term performance through an understanding of the mechanism whereby polarization is lost at elevated temperatures. Investigations are continuing on the factors which influence the stability such as poling conditions, crystal structure, chemical structure, and molecular motions. Concurrent with these investigations, we are working with research associates to disseminate the knowledge gained. We are also fabricating, calibrating, and employing polymer transducers in new measurement systems for other government agencies.

Although polymers have long been used for their insulating properties, electronic conduction and ionic conduction in polymers is an exciting new area of solid state physics. Ionic transport in polymers provides the basis for a large and growing class of important applications including the production of chlorine and sodium hydroxide from the electrolysis of brine, hydrogen production from low-head hydroelectric sources, solid electrolytes for fuel cells and batteries, materials separation membranes and electrochemical sensors. In most such applications, it is required that the current be carried entirely by ions participating in an electrochemical reaction rather than by electrons which essentially short-circuit the cell. NBS work involves the preparation of ion-conducting specimens, measurement of transport properties, measurement of electrical properties, characterization of structure, and relating the structure and properties to provide a basis for transport mechanisms at the molecular level. These concepts will then guide the development of ion-transporting films with improved conductivity.

Automated Dielectric Measurements
Subtask 1 of Task 15439

F. I. Mopsik

This activity was undertaken to provide efficient, rapid and accurate measuring systems for the measurement of dielectric constant and loss at audio and subaudio frequencies.

The main work up until now has been the development of a time domain dielectric spectrometer which records the transient electric charge response to an applied voltage for times from 10 μs to 3000 s. This response is then numerically transformed into an equivalent frequency range of 10^{-4} to 10^{4} Hz. The basic accuracy of the instrument is 0.1% with a loss resolution of better than 10^{-5} in tan δ.

In FY 84, the basic paper describing the instrument was published in the Review of Scientific Instruments. An invited talk at the meeting of the Dielectrics Society in Reading, United Kingdom was also given. Support was maintained with the research associates at IMASS, Inc. and General Electric who are proceeding to duplicate the instrument. The one from IMASS is intended for commercial introduction. Both machines are now well into the construction phase and a beginning has been made to set up test protocols to verify the performance of the instruments.

As a further step in the utilization of the spectrometer, modifications are being considered to allow the sequencing of measurements under the control of a real-time clock so that time studies can be made for such purposes as the curing of epoxy resins and the aging of amorphous polymers. It is expected that such a development will bring out the advantages of speed and accuracy of the spectrometer.

Dielectric Properties of Polyvinylidene Fluoride

Subtask 2 of Task 15439

A. J. Bur and F. I. Mopsik

This subtask directly supports the optimization of piezoelectric polymers for applications in industry and government. It concerns the definition of PVDF properties prior to poling which, after poling, will yield highly active transducers with optimum ageing characteristics.

Previous work has shown that the loss peak at 1 Hz at 30 °C is not associated with the α-form crystals in PVDF. This was based on the combination of x-ray orientation studies on drawn material and the measurement of the magnitude of the dispersion after drawing. In addition, a compensation was found in that the decrease, but not disappearance, of the 1 Hz loss peak corresponded with an increase in the intensity of loss at 10^6 Hz that has been tied to the amorphous phase. Also, these changes have been found to be too large to be accounted for by orientation of the amorphous phase.

Work in FY 84 has been shifted to the loss centered near 10^{-2} Hz. This loss region has been found to have a characteristically very flat maximum. It is found to arise only upon orientation of α-phase material and seems not to be present in unoriented polymer, although a strong 1 Hz loss peak makes detection difficult. Previously, it was noted that the intensity of this loss was quite variable. A series of samples were prepared using different draw rates and draw temperatures to investigate possible origins of this loss. It was found that the intensity was only mildly influenced by temperatures of 125° - 140 °C and draw rate of 0.1 to 1 cm/min. A sample drawn at 150 °C showed behavior intermediate between the drawn and undrawn material with respect to 1 Hz loss helping to confirm earlier measurements. However, we have still not been able to establish the conditions necessary for influencing the magnitude of the 10^{-2} Hz loss region.

Dielectric and Acoustic Phantoms

Subtask 3 of Task 15439

M. G. Broadhurst

The calibration and testing of devices which subject the human body to high frequency electromagnetic or ultrasonic radiation requires materials (called a phantom) which duplicate the dielectric or acoustic and thermal properties of living human tissues. Presently-used phantoms are aqueous gels containing a large fraction of water with dissolved and dispersed substances such as salts, aluminum powders and polyethylene powders. These gels are unstable because of bacteria attack, loss of water and chemical reactions. This project, sponsored by the Bureau of Radiological Health, seeks a new type of phantom material which will have improved stability without loss of desirable properties.

So far, work has focused on the dielectric phantom. Some of the activities related to this phantom are:

1. We made dielectric measurements on live plant leaves as a convenient analog to animal tissue. Both respond primarily as cells containing salt water, with bulk properties dominant at 100 MHz and interfacial properties becoming important at 1 MHz.

2. We made measurements on single crystal silicon which has a dependence of ε' and ε'' on frequencies from 1 to 100 MHz nearly identical to that of leaves. The important point here is to establish the difference between these two materials. It seems likely at this point that one could have a material with the same apparent ε' and ε'' as tissue but with the dielectric heating occurring on the surface rather than in the bulk of the material. One must match not only ε' and ε'' but also the distribution of dielectric heating within the sample.

3. We made a survey of thermal properties of materials. It seems that a reasonable match of thermal diffusivity between polymers and tissue can be expected. Blood circulation will have a large effect on tissue which we do not expect to match.

4. We prepared polyvinyl chloride gels and procured a number of high dielectric constant plasticizers. We are examining carbon-black as the most suitable filler to give the desired dielectric properties and the PVC system is quite convenient. We also obtained some ceramic ferroelectric fillers but expect these to produce a material that is fairly dense and hard. The problem is in getting enough filler in the polymer to give a sufficiently high dielectric constant without producing undesirable properties.

5. We contacted commercial fabricators and suppliers of polymer-carbon black composites to help identify convenient suppliers. The type of material we envision for the phantom is that used to make artificial fishing worms but with the appropriate loading.

6. We are doing a theoretical study of the diffusion of interacting charged particles in a material under an applied field. This should establish the significance of various parameters in determining the interfacial contributions to the dielectric properties. This study is crucial in separating effects of space charge and interfacial polarization.

The final report will provide a fairly detailed and documented description of the dielectric behavior of tissue and of tissue-phantom materials. Experimental data will be provided on the carbon-black and ferroelectric ceramic PVC gel system as well as the silicon and tissue systems.

Work on the acoustic phantom is to follow similar lines as above. The location of the glass transition temperature which depends on polymer structure and plasticizer, is crucial in the absorption coefficient.

Fundamental Studies of Conducting Polymers

Subtask 4 of Task 15439

C. K. Chiang

Electrically conducting polymers is a new area of research of materials in which many organic systems have potential for lightweight and electroactive applications. Novel properties found in this class of material have stimulated much academic and applied interest. This task continues the effort to explore the fundamental nature of conducting polymers. We have examined the mechanism for electrochemical doping of polyacetylene, $(CH)_x$.

The high electrical conductivity of polyacetylene can also be accomplished by electrochemical method of doping. Since electrical current and potential can be easily controlled, the resulting polymer will be easier to specify than other doping methods such as exposing to gas. Also, the electrochemical reactions of polyacetylene are the basis for its application as a lightweight battery. Our investigation is an attempt to understand this novel behavior.

The concept of doping is borrowed from the field of conventional semiconductors. It is used to describe the changes in electronic structure of the polymer due to a small amount of added chemical impurities. In conducting polymers the dopant concentration is much higher than that found in the conventional semiconductor but the resulting properties appears to be similar. From the electrochemical point of view, a dopant oxidizes or reduces the host polymer. When such a process makes the polymer conducting, the charge must be distributed over long segments of the chain rather than being localized as in conventional redox processes. The doping of polyacetylene may therefore be a new type of redox phenomena.

We measured the cyclic voltammogram of $(CH)_x$ at a platinum electrode. Two different film thicknesses were investigated. The I-V curve of a thin $(CH)_x$ film (<1 μm) electrode exhibited a redox peak with a formal redox potential of +0.65 V vs. sodium calomel electrode. Approximately 30% of the total charge that oxidized $(CH)_x$ was not reversible when held at the open circuit voltage of the cell. A more negative potential was needed to recover the remaining charge. This large charge-trapping phenomenon was the consequence of the $(CH)_x$ film being doped. Using a thick film (≥50 μm) electrode or freestanding film (~0.1 mm) as an electrode, the I-V curve gave only a broad re-reduction peak at +0.4 V. The disappearance of the well-defined redox peak implies that the redox process revealed by the thin film data may not be the predominate mechanism for the doping process.

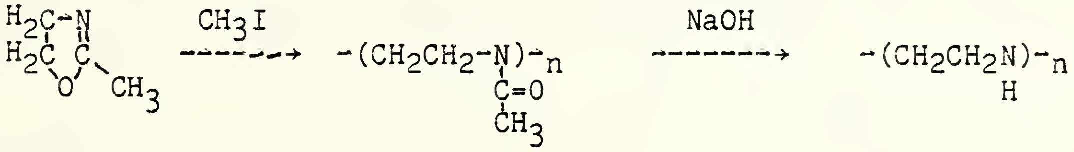
Ion Transport in Solid Polymers

Subtask 5 of Task 15439

C. K. Chiang, G. T. Davis, C. A. Harding, and T. Takahashi[1]

[1] Guest worker from Ube Industries, Japan

We have synthesized linear polyethylene imine (PEI) using the polymerization procedure described by Saegusa et al. Methyl iodide was used to initiate the ring opening polymerization of 2-methyl oxazoline in dimethyl formamide to yield poly(N-acetyl-ethylene imine). Linear PEI was produced by hydrolyzing poly(n-acetyl-ethylene imine) with NaOH.



The synthesis procedure is simple but time consuming, especially in those steps involving oxygen free conditions, washing the products and removing the solvents. One complete preparation (~10 gm of PEI) required as long as one month. In order to supply experimental needs, we have developed a scale-up method which is able to produce ~100 gm.

The PEI was characterized using differential scanning calorimetry, x-ray diffraction and FTIR and results are in good agreement with published data. The molecular weight of linear PEI measured by GPC method is ~2000. It is in the same range as those obtained by Saegusa. Some effort will be directed to produce linear PEI with higher molecular weight, which can provide oriented PEI for more detailed studies.

By analogy to PEO, we have made mixtures of sodium iodide and PEI. The DSC studies were made to follow the thermal behavior of this mixture. When the concentration of the salt (in terms of the ratio of salt to ethylene imine units) increases from 0 to 1, we observed a sudden increase of melting point at concentration 0.30. Below c=0.30 the melting point of the mixture is in the vicinity of 50 °C. Above c=0.3 the melting point of the mixture is 150 °C. This increase of melting point is an indication of forming a salt-polymer complex at this ratio. X-ray patterns of PEI-0.30 NaI complex revealed a new x-ray pattern which is different from the original PEI. The DSC behavior and structure change resemble those found in the PEO system.

Polyethylene oxide (PEO) is the prototype polymer that exhibits ionic conducting properties. PEI provides another linear polymer system in which the -NH- replaces an -O- in the backbone structure. We plan to continue investigation of conductivity in this polymer-salt system.

Structure and Performance of Piezoelectric Polymers

Subtask 6 of Task 15439

G. T. Davis and M. G. Broadhurst

The objectives of this task are to study the molecular motions, structural changes, and electrical properties associated with the process whereby polymers are made piezoelectric. Information gained from these studies will be used to optimize piezoelectric and pyroelectric response with respect to both initial activity and long-term stability.

Some polymers (most notably, polyvinylidene fluoride) can be made piezoelectric and pyroelectric by the temporary application of high electric fields. We have shown that the response arises from changes in the residual polarization which results from the field-induced alignment of dipoles in the polymer crystallites. Recent analyses indicate that changes in thickness of the polymer film contribute about 2/3 of the piezoelectric activity and the remaining 1/3 of the activity is attributed to changes in the dipole moment of the film at constant thickness. Eight separate possible contributions to the change in moment have been proposed but each is difficult to evaluate.

The influence of chemical composition on crystal structure and resultant piezoelectric properties is evidenced by a series of copolymers of vinylidene fluoride and trifluoroethylene. Copolymers containing between 50 and 85 mole percent vinylidene fluoride crystallize primarily in a polar crystal form and undergo a ferroelectric to paraelectric transition at a temperature which increases with increasing concentration of vinylidene fluoride. The dipoles can be oriented at values of electric fields on the order of one-half of those required for polyvinylidene fluoride and piezoelectric activity is comparable to that of the homopolymer even without aligning the polymer chains by drawing. The loss of polarization as a function of temperature is being examined in these copolymer systems as part of our investigation on the factors governing the long term stability of polymeric transducers.

Polarization and Space Charge Studies

Subtask 7 of Task 15439

A. S. DeReggi and F. I. Mopsik

The thermal pulse technique has been developed in this laboratory for studying the distribution of permanent polarization across the thickness of a dielectric film. This measurement method has provided key information in understanding the poling behavior of polymeric materials used as piezo- and pyroelectric elements.

During the past year, the technique has been successfully applied to films of PVC and PTFE subjected to electron irradiation in which one determines the distribution of charge as opposed to polarization. [In the case of PVC, we observe a polarization which must have resulted from internal fields set up by the injected electrons.] A time-averaging capability has been added to the system for studying samples which exhibit a low signal to noise ratio.

We expect the technique to play a dominant role in measuring the distribution of charge in insulating films subjected to DC fields in a future study on dielectric break-down. The measurement of small amounts of charge very near the surface requires that the duration of the light pulse be decreased and the power increased over that of the photographic flash unit currently employed.

A Dynamic Polymer Pressure Transducer With Temperature Compensation

Subtask 8 of Task 15439

A. J. Bur and S. C. Roth

At the request of the U. S. Air Force and the Defense Nuclear Agency, pressure gauges using polyvinylidene fluoride (PVDF) are being developed for the purpose of measuring dynamic pressures in air and in various underground soil environments

Since PVDF is both piezoelectrically and pyroelectrically active, accurate pressure measurements can be made either for an isothermal situation or when the appropriate temperature compensation is applied to the charge output of the gauge. One of the principle sources of thermal energy in or in the neighborhood of the gauge is adiabatic compressional heating during the event of a pressure pulse. In PVDF, the effect of adiabatic compressional heating is small, approximately an 8% effect, and it can be neglected or incorporated into the calibration procedure. In soil the effect is also small and can be neglected in most cases. But in air it is a large effect for which compensation is necessary. Other sources of thermal energy can be internal friction, radiation or some source peculiar to the measurement.

The PVDF transducer is made from four sheets or films of polymeric material which are laminated together using epoxy. The inner two films are each 12 or 25 μm thick PVDF and each contain a piezoelectrically active region 1 cm in diameter. Electrodes, 10^2 nm indium on top of 10^2 nm aluminum, are placed on the PVDF films using a vacuum deposition process. The outer two layers, whose thickness is adjusted in order to achieve a particular value of τ, the thermal time constant, can be PVDF or another polymeric material such as polycarbonate. A commercial copper-constantan thermocouple, made with 12 μm metal strips, is placed between the inner two sheets and within 2 mm of the active transducer area.

To analyze the thermal effect on the pressure measurement, we consider the thermal time constant, τ, for the conduction of heat into the transducer from its surroundings. If τ is large and the measurement is made at times $t \ll \tau$, then the temperature affect can be avoided. If, on the other hand, $t \lesssim \tau$ or $t > \tau$, the temperature change of the gauge must be measured in order to apply the appropriate correction to its electrical signal.

Since τ depends on the dimensions of the transducer, it is often possible to adjust τ in accordance with the requirements of the measurement. For thin film transducers, τ, as determined from the solution to the heat flow equation in one dimension, depends on the square of the thickness, ℓ, of the transducer. For a PVDF transducer with $\ell = 0.7$ mm, $\tau \approx 1$ s; accurate pressure measurements for $t < 0.05$ s ($\tau/20$) would be possible without active compensation. For some applications it is not appropriate to change ℓ in order to accommodate the time scale of the measurement. For this situation, i.e. $t \leqq \tau$ or $t > \tau$, we have developed a temperature compensated pressure transducer. Compensation is achieved by using the voltage output from the thermocouple which is amplified in accordance with the pyroelectric response of the PVDF; it is then added to the transducer signal in order to achieve temperature compensation. A circuit which amplifies and adds the thermocouple and transducer signals has been designed and tested. Its output voltage is proportional to pressure and its dynamic range is 0.1 Hz to 10^5 Hz.

Two experiments are used to calibrate the transducers. One is designed to investigate transducer response to pressure changes in the time regime, $t \leqq \tau$ or $t > \tau$, and the other is concerned with $t \ll \tau$. For the first case, the transducer is placed in an oil pressure chamber and is subjected to pressure pulses having a peak value up to 2.8×10^7 Pa (4000 psi) and a half width of 10 ms. Adiabatic compressional heating causes a pyroelectric response which is approximately 15% of the total charge output of the transducer. Compensation is achieved using the compensation circuit. For the second case, $t \ll \tau$, the transducer is placed in an air pressure chamber in which the pressure of the air is changed in a step function manner at time $t = 0$ and held constant at a constant value for $t > 0$. We observe that the charge output of the transducer remains constant indicating a constant value of pressure as long as $t \leqq \tau/20$. At longer times, the effect of temperature causes a change in the transducer charge measurement, so that the calibration is applicable only at times $t \leqq \tau/20$.

These transducers were used in field tests at Eglin Air Force Base. The tests consisted of measuring dynamic pressures underground at the base of a concrete bunker and inside the bunker in air. The pressures were generated by small explosives. The gauges were found to operate satisfactorily and yielded data which were in agreement with other measurements.

One report and two archival journal articles which describe the development and use of this gauge have been written.

Polymeric Pressure Transducers for Printing Presses
Subtask 9 of Task 15439

S. C. Roth and A. S. DeReggi

During the past few years, we have worked with the Bureau of Engraving and Printing in studying the feasibility of using piezoelectric polyvinylidene fluoride films for measuring the pressure to which currency is subjected when it passes through the nip of an intaglio press. As an outgrowth of this work, we have provided BEP with calibrated pressure gauges, associated amplifiers, and rotating electrical contacts especially designed to fit on a web-fed press at the Denmark National Bank and a sheet-fed press at the Bank of England. The piezoelectric films give reproducible results on successive passes through the nip indicating pressures as high as 40,000 psi (2.8×10^8 Pa) with pulse width on the order of 0.01 seconds. Unfortunately, the fragile electrical connections to the polymer thin films were destroyed after only a few tests. Although the total thickness of the gauges was on the order of 50 μm, even this thickness causes an appreciable perturbation on the pressure that material experiences when passing through the nip. However, when placed at different locations on the cylinder, the gauges proved very useful in indicating non-uniform pressure distributions during the printing process.

Diffusion of Ethyl Acetate Vapor in Polyvinylidene Fluoride

Subtask 10 of Task 15439

J. C. Phillips and G. T. Davis

Studies of the diffusion of small molecules in semicrystalline polymers lead to the conclusion that transport occurs only within the amorphous regions. Polyvinylidene fluoride (PVDF) is a semicrystalline polymer in which the crystal structure can be changed by the temporary application of high electric fields (poling) which is expected to have very little effect on the structure of the amorphous phase. Yet, we find that poling greatly reduces the rate of transport of ethyl acetate vapor in a poled polymer film without altering the equilibrium uptake. These studies are being extended to copolymers of vinylidene fluoride and trifluoroethylene which exhibit a crystal-crystal transition and thermal depoling at temperatures far below the melting point which again should have minimal effects on the amorphous component. We hope to determine whether the changes in transport properties which we observe are caused by structural changes within the amorphous phase, by the presence of polar crystals, by charges trapped within the film, or some other effect.

Ferroelectric Polymers: Modeling of Ferroelectric Polarization in Polyvinylidene Fluoride

Subtask 11 of Task 15439

D. H. Reneker

This work was undertaken to provide a basis for the optimization of the polarization process in ferroelectric polyvinylidene fluoride films which are finding widespread application as transducers and thermal radiation detectors.

Ferroelectric polarization of the beta phase of polyvinylidene fluoride involves mechanical extension of the specimen and application of an external electric field in a direction perpendicular to the molecular axis and to the polymer film. A model for the mechanism of polarization is investigated, based on the propagation of twist boundaries at which all the chains are twisted by 180 degrees. These boundaries separate domains of opposite polarization.

It was found that, under poling conditions most commonly employed, the poling force is large enough to overcome the potential barrier that impedes the free movement of the twist boundary. The motion of the twist boundaries in response to the applied electric field provides a model for the poling of the beta phase of polyvinylidene fluoride and probably also of other ferroelectric polymers, which is both feasible energetically and kinematically. Theoretical modeling suggests that this polarization process can be described either as diffusion of a boundary or as propagation of a soliton along the molecular chains.

Invited Talks

Low Surface Energy Dental Composites from a Polyfluorinated Prepolymer Multifunctional Metacrylate
Society of Plastics Industry
New Brunswick, NJ
J. M. Antonucci
October 1983

New Developments in Composites and Adhesion
Greater NY Dental Meeting
New York City
R. L. Bowen
November 1983

Dentinal Adhesives
Conf. for Teachers of Dental Materials
Morgantown, WV
R. L. Bowen
November 1983

Consensus Development Conference on Dental Sealants in the Prevention of Dental Caries-Safety Considerations, Oral and Systemic
Consensus Development Conference
Bethesda, MD
R. L. Bowen
December 1983

Bonding of Composites to Dentin and Enamel In Vitro
Georgetown University
Washington, DC
R. L. Bowen
January 1984

Advancements in Methods to Bond Composites to Dentin
Academy of Operative Dentistry Annual Meeting
Chicago, IL
R. L. Bowen
February 1984

Smear Layer: Removal and Bonding Considerations
Intl. Assn. for Dental Research, Smear Layer Symp.
Dallas, TX
R. L. Bowen
March 1984

Adhesive Bonding of Composites to Dentin
Dental Students Res. Conference
Bethesda, MD
R. L. Bowen
March 1984

Improved Method to Obtain Adhesion of Composites to Dentin
Nassau County Dental Society
Uniondale, NY
R. L. Bowen
May 1984

Adhesion of Composites to Dentin
Pierre Gauchard Academy Japanese Section
Tokyo, Japan
R. L. Bowen
July 1984

Adhesion of Composites to Dentin
Nihon University School of Dentistry
Tokyo, Japan
R. L. Bowen
July 1984

Adhesion of Composites to Dentin
Tokyo Medical and Dental University
Tokyo, Japan
R. L. Bowen
July 1984

Adhesion of Composites to Dentin
Tokushima University, School of Dentistry
Tokushima, Japan
R. L. Bowen
July 1984

Adhesion of Composites to Dentin
Aichi-Gakuin University
Nagoya, Japan
R. L. Bowen
July 1984

Adhesion of Composites to Dentin
National Taiwan University of Dentistry
Taipei, Taiwan
R. L. Bowen
July 1984

Bonding of Restorative Materials to Dentin: Principles and Problems. What is the Present Status in the United States
72nd Annual World Congress
Federation Dentaire International
Helsinki, Finland
R. L. Bowen
August 1984

The Structure and Morphology of Polyurethanes
New Mexico Inst. of Mining & Tech., Dept. of Metallurgy
and Materials
Socorro, NM
R. M. Briber, Jr.
May 1984

Dielectric Properties of PVDF
Eastman Kodak Co.
Rochester, NY
M. G. Broadhurst
October 1983

A Summary of Piezoelectric and Pyroelectric Applications of Polymers
American Physical Society Meeting
San Franciso, CA
M. G. Broadhurst
November 1983

PVDF Pressure Transducers
Eglin Air Force Base
Fort Walton Beach, FL
A. J. Bur
June 1984

Calorimetry of the Vitreous State
National Tsing Hua University
Taiwan
S. S. Chang
October 1983

Diffusion and Migration of Low Molecular Weight Substances from
Polymers
Chung San Inst. of Science & Technology
Taiwan
S. S. Chang
October 1983

Topical Fluoridation of Teeth
National Institute of Dental Research
Rockville, MD
L. C. Chow
October 1983

Sodium Iodide Conductivity in Polyethylene Oxide & Polyethylene Imine
DoE and ONR sponsored Workshop on Conducting Polymers
Detroit, MI
G. T. Davis
June 1984

Piezoelectricity, Pyroelectricity and Ferroelectricity in Synthetic Polymers
College of William & Mary
Williamsburg, VA
A. S. DeReggi
September 1984

Low Fusing Ceramics in Dentistry
Materials Research Lab. Conf. on Chemically Bonded Ceramics
University Park, PA
W. G. deRijk
July 1984

Factors Affecting Photodegradation in Polymethyl Methacrylate
American Chemical Society Meeting
Newark, NJ
B. Dickens
May 1984

Field Theory, Curdling, Limit Cycles and Cellular Automata
Fractals Conference at NBS
Gaithersburg, MD
E. A. Di Marzio
November 1983

Structure Inducing Phase Transition Phenomena
NBS Research Staff Seminar
Gaithersburg, MD
E. A. Di Marzio
January 1984

Chain Statistics in Rubbers, Glasses and Polymer Lattices
University of Maryland Lecture Series
College Park, MD
E. A. Di Marzio
January 1984

Structure Inducing Phase Transitions in Polymers
Dept. of Physics & Astronomy
Howard University
Washington, DC
E. A. Di Marzio
April 1984

Structures and Transitions in Polytetrafluoroethylene
Lehigh University
Bethlehem, PA
R. K. Eby
November 1983

The High Pressure Phase of Polytetrafluoroethylene
Virginia Polytechnic Institute
Blacksburg, VA
R. K. Eby
April 1984

Analysis of IR Spectra from Polyethylene-Polyethylene-d_4 Mixtures
Case Western Reserve University
Cleveland, OH
B. M. Fanconi
November 1983

Cure Monitoring of Polymer Composites
Army Materials Research Conference
Lake Luzerne, NY
B. M. Fanconi
August 1984

Trends in Polymer Development and Analytical Techniques
Intl. Symp. on Analysis and Identification of Polymers
FBI Training Academy, Quantico, VA
B. M. Fanconi
August 1984

FTIR Studies of Molecular Organization in Polyethylene
ACS Symp. on FTIR Characterization of Polymers
Philadelphia, PA
B. M. Fanconi
August 1984

Advanced Characterization Techniques Applied to Molecular Composites
Department of the Air Force
Dayton, OH
B. M. Fanconi
September 1984

A Review of the Thermal and Oxidative Degradation of Polymers
Center for Fire Research Seminar
NBS, Gaithersburg, MD
J. H. Flynn
March 1984

Investigation of the Cure of Ink and Drying Oils by Differential Scanning Calorimetry
BEP, Office of Research & Technical Services
Washington, DC
J. H. Flynn
June 1984

Application of Analytical Pyrolysis to Interpretation of Polymer Degradation Mechanisms and Vice Versa
13th North American Thermal Analysis Society Conference
Philadelphia, PA
J. H. Flynn
September 1984

Fracture Mechanics of Elastomeric Composites
Gordon Research Conference on Composites
Santa Barbara, CA
A. N. Gent
January 1984

Failure Processes in Elastomers at and Near a Rigid Inclusion
DoD Polymer Conference
Asilomar, CA
A. N. Gent
February 1984

Strength of Elastomers
Lawrence Livermore National Laboratory
Livermore, CA
A. N. Gent
February 1984

Fracture of Elastomeric Composites
Technical Lecture Series
E. I. duPont de Nemours and Co., Inc.
Wilmington, DE
A. N. Gent
March 1984

Analysis of Fracture of Model Composites
Center for Applied Mathematics Colloquium Series
NBS, Gaithersburg, MD
A. N. Gent
April 1984

Monte Carlo Studies of Two Measures of Polymer Chain Size as a Function of Temperature
Third Conference on Fractals in the Physical Sciences
NBS, Gaithersburg, MD
G. M. Guttman
November 1983

Dynamic Light Scattering of Polymers in the Intermediate q-Region
Gordon Research Conference
Los Angeles, CA
C. C. Han
January 1984

Dynamic Light Scattering from Semi-Dilute Polymer Solutions
University of Massachusetts
Amherst, MA
C. C. Han
March 1984

Dynamic Light Scattering from Polymer Solutions
American Physical Society
Detroit, MI
C. C. Han
March 1984

Neutron Cloud Point and Critical Fluctuation of Polymer Blends
American Physical Society
Detroit, MI
C. C. Han
March 1984

Polymer Conformation by Small Angle Neutron Scattering
University of Minnesota
Minneapolis, MN
C. C. Han
May 1984

Critical Fluctuation and Phase Separation of Polymer Blends by SANS
University of Wisconsin
Madison, WI
C. C. Han
May 1984

Structure of Glassy Polymers by Neutron Scattering
The Interdisciplinary Workshop on the Structure and Properties of Amorphous Solids
Williamsburg, VA
C. C. Han
June 1984

Dynamic Light Scattering from Polymer Solutions
"Stockmayer 70th Birthday Symposium"
Dartmouth College
Hanover, NH
C. C. Han
July 1984

The Morphology of Poly(ethylene Terephthalate) Fibers as Studied by Multiple-Pulse Proton NMR
GTE Laboratories, Inc.
Waltham, MA
J. R. Havens
October 1983

The Morphology of Poly(ethylene Terephthalat) Fibers as Studied by Multiple-Pulse Proton NMR
Polymers Division Seminar
Gaithersburg, MD
J. R. Havens
March 1984

The Morphology of PET Fibers as Studied by Multiple-Pulse Proton NMR
AT&T Bell Laboratories
Murray Hill, NJ
J. R. Havens
March 1984

Diffusion of Fluorescent Additives in Polyethylene
American Chemical Society
Bethesda, MD
B. F. Howell
February 1984

Failure Behavior of Tough Polymers for Composites and Adhesives
Seminar for Composite Resins Laboratory
Hercules Research Center
Wilmington, DE
D. L. Hunston
January 1984

Fundamental Aspects of Adhesion
Workshop on Engineering with Adhesives
East Brunswick, NJ
D. L. Hunston
January 1984

Mechanical Properties of Compliant Coating Materials
ASME Symp. on Laminar/Turbulent Boundary Layers
New Orleans, LA
D. L. Hunston
February 1984

Fracture of Polymeric Adhesives
Workshop on Adhesion, Matls. Tech. Division
Los Alamos National Laboratory
Los Alamos, NM
D. L. Hunston
February 1984

Failure Behavior of Elastomer-Modified Epoxy Adhesives
Adhesives, Coatings, and Sealers Division
3M Company
St. Paul, MN
D. L. Hunston
April 1984

Failure Behavior of Tough Polymers for Composites and Adhesives
University of Illinois
Urbana, IL
D. L. Hunston
April 1984

Polymer Composites-A Scientific Approach to Process Control
NBS Staff Research Series
Gaithersburg, MD
D. L. Hunston
April 1984

Fracture Behavior of Glassy Adhesives
Workshop on Principles and Practices of Adhesive Bonding
Kent, OH
D. L. Hunston
May 1984

The Role of Adhesion Science in Composite Delamination
Workshop of Center for Adhesion Science
Virginia Polytechnic Institute
Blacksburg, VA
D. L. Hunston
May 1984

Toughening of Polymers
Annual Meetin of the Society of Polymer Science
Nagoya, Japan
D. L. Hunston
May 1984

Fracture Properties of Composites and Adhesives
Department of Polymer Chemistry, Kyushu University
Hakata, Japan
D. L. Hunston
June 1984

Fracture Behavior of Polymers
UBE Industries
Hirakata Plastics Laboratory
Osaka, Japan
D. L. Hunston
June 1984

Tough Polymers for High Performance Applications Like Composites and Adhesives
E. I. DuPont de Nemours, Dupont Experimental Station
Wilmington, DE
D. L. Hunston
August 1984

Viscoelastic Fracture Behavior for Different Rubber-Modified Epoxy Adhesive Formulations
The International Adhesion Conference 1984
Nottingham, England
D. L. Hunston
September 1984

Simultaneous Measurement of Torque and Normal Force During Physical Ageing of PMMA
Polymers Division Seminar
Gaithersburg, MD
G. B. McKenna
November 1983

On the Time Dependent Failure Behavior of Polymeric Materials
Imperial College of London
London, England
G. B. McKenna
December 1983

The Behavior of Natural Rubber Vulcanization at Extremely Small Deformations
Centre de Recherches sur les Macromolecules
Strasbourg, France
G. B. McKenna
December 1983

Simultaneous Measurement of Torque and Normal Force as Probes of Physical Ageing in Glassy Polymers
Universite de Pau et des Pays del-Adour
Pau, France
G. B. McKenna
December 1983

Simultaneous Measurement of Torque and Normal Force in Torsion in the Study of Constitutive Laws
Universite P. Sabatier
Toulouse, France
G. B. McKenna
December 1983

Physical Ageing of a Thermoplastic Resin in the Non-linear Deformation Range
Gordon Conference on Composites
Santa Barbara, CA
G. B. McKenna
January 1984

Simultaneous Measurement of Torque and Normal Force Responses as Probes of Physical Ageing in Glassy Polymers
IBM Research Laboratories
San Jose, CA
G. B. McKenna
January 1984

Measurement of the Small Strain Behavior of Peroxide Cured Natural Rubber in Torsion, Extension and Compression
University of Pittsburgh
Pittsburgh, PA
G. B. McKenna
June 1984

On the Small Strain Behavior of Peroxide Cured Natural Rubber
Gordon Research Conference
New London, NH
G. B. McKenna
July 1984

Wear Mechanisms of Dental Composite Restoratives
University of Maryland, Dental School
Baltimore, MD
J. E. McKinney
April 1984

The Dielectric Behavior of PVDF
University of Leeds
Leeds, England
F. I. Mopsik
April 1984

Time-Domain Measurements and Its Application of PVDF
Dielectrics Society Meeting
Reading, England
F. I. Mopsik
April 1984

Transport in Disordered Systems: A Fractal View
Symposium on Fractals in the Physical Sciences
NBS, Gaithersburg, MD
R. J. Rubin
November 1983

Average Properties of Weighted Random Walks and Reflecting Boundary Conditions
Rutgers University
New Brunswick, NJ
R. J. Rubin
December 1983

Random Walk Models for Counting Polymer Chain Configurations
Rutgers University
New Brunswick, NJ
R. J. Rubin
March 1984

Weighted Random Walks and Polymer Chain Configurations
Polymer Science & Engineering Department
University of Massachusetts
Amherst, MA
R. J. Rubin
September 1984

Pulp Considerations in Operative Dentistry
U. S. Air Force Surgeon General
Saginaw, MI
N. W. Rupp
October 1983

Recent Developments in Esthetic Dentistry - Bonding
Florida Panhandle Dental Society
Ft. Walton Beach, FL
N. W. Rupp
October 1983

Recent Developments in the Selection and Handling of Dental Materials
U. S. Air Force Surgeon General
Eglin AFB, FL
N. W. Rupp
October 1983

Recent Developments in Impression and Die Materials
United States Navy
Bethesda, MD
N. W. Rupp
November 1983

Recent Developments in the Cementation (Pulp Response & Materials)
United States Navy
Bethesda, MD
N. W. Rupp
December 1983

Amalgam and Bonding of Composites
United States Navy
Bethesda, MD
N. W. Rupp
January 1984

Recent Developments in Dental Materials
U. S. Naval Dental School
Bethesda, MD
N. W. Rupp
February 1984

Discussion of Amalgam Materials, Their Handling & Application
Academy of Operative Dentistry
Chicago, IL
N. W. Rupp
February 1984

Dental Amalgam
University of Maryland
Baltimore, MD
N. W. Rupp
February 1984

Operative Procedures and Pulp Protection, Amalgam & Composites
Georgetown University School of Dentistry
Washington, DC
N. W. Rupp
April 1984

The Hazards of Mercury
Minnesota State Dental Society
Minneapolis, MN
N. W. Rupp
April 1984

The Hazards of Mercury and Compacting Dental Amalgam
Academy of Gold Foil Operators
Winnipeg, Manitoba, Canada
N. W. Rupp
April 1984

Improved Method to Obtain Adhesion by Composites to Dentin
Nassau County Dental Society
Uniondale, NY
N. W. Rupp
May 1984

Clinical Experiences of Biocompatibility of Metals in Dentistry, Biological Aspects
Workshop on Biocompatibility of Metals in Dentistry
American Dental Association
Chicago, IL
N. W. Rupp
July 1984

The Amalgam Controversy
University of Texas
San Antonio, TX
N. W. Rupp
August 1984

Selection and Use of Recently Developed Dental Materials
Ohio Dental Association
Columbus, OH
N. W. Rupp
September 1984

Callahan Memorial Award Response, Composites: State-of-the-Art
Ohio Dental Association
Columbus, OH
N. W. Rupp
September 1984

Amalgam Controversy: Point-Counterpoint
Ohio Dental Association
Columbus, OH
N. W. Rupp
September 1984

Statistical Thermodynamic Aspects of Polymer Blends
University of Maryland
College Park, MD
I. C. Sanchez
November 1983

Polymer Blend Trilogy: Thermodynamics, Diffusion and Interfaces
B. F. Goodrich Res. & Dev. Center
Brecksville, OH
I. C. Sanchez
December 1983

Polymer Blend Trilogy: Thermodynamics, Diffusion and Interfaces
Society of Plastics Engineers, Stanford Res. Institute
Stanford, CA
I. C. Sanchez
January 1984

Invariant Properties of Liquids: A New Discovery?
Chemical Engineering Department, Stanford University
Stanford, CA
I. C. Sanchez
January 1984

Aspects of Polymer Interphases and Interfaces
Polymers Gordon Conference
Santa Barbara, CA
I. C. Sanchez
January 1984

Interfacial Properties of Polymer Liquids, Solutions and Blends
American Physical Society
Detroit, MI
I. C. Sanchez
March 1984

Corresponding States in Polymer Solutions and Blends
Intl. Symp. on Polymer Alloys: Structure & Properties
Brugge, Belgium
I. C. Sanchez
June 1984

Phase Diagrams of Polymer Solutions and Blends
Imperial College
London England
I. C. Sanchez
June 1984

A Universal Coexistence Curve for Polymer Solutions
Cavendish Laboratory
Cambridge, England
I. C. Sanchez
June 1984

Polymer Blend Trilogy: Thermodynamics, Diffusion and Interfaces
Eastman Kodak Research Labs.
Kingsport, TN
I. C. Sanchez
August 1984

Polymer Blend Trilogy: Thermodynamics, Diffusion and Interfaces
Phillips Petroleum
Bartlesville, OK
I. C. Sanchez
August 1984

Liquids: Surface Tension, Compressibility and Invariants
University of Delaware
Newark, DE
I. C. Sanchez
September 1984

Thermodynamic & Interfacial Properties of Polymer Blends
Northwestern University
Evanston, IL
I. C. Sanchez
September 1984

Contrasts in Research: Basic vs. Applied & Industrial vs. Government
Chemical Society of Washington
Washington, DC
G. A. Senich
October 1983

Measurements of Diffusion in Polymers by Inverse Gas Chromatography
Hercules Inc.
Wilmington, DE
G. A. Senich
July 1984

Cure Kinetics Measurements on Polymer Composite Matrix Materials
American Chemical Society
Philadelphia, PA
G. A. Senich
August 1984

Predicting Lifetime of Polymers
Johns Hopkins University
Baltimore, MD
L. E. Smith
April 1984

Chemistry and Material Needs
American Chemical Society Centennial Symposium
University of Maryland
College Park, MD
L. E. Smith
May 1984

A Quantitative/Expedient Porcelain Fused-to-Metal Bond Test:
Theoretical Basis and Experimental Basis
Northwestern University
Chicago, IL
J. A. Tesk
November 1983

Characterization of Porcelain Fused-to-Metal Systems
Tokyo Medical & Dental University
Tokyo, Japan
J. A. Tesk
November 1983

The Promise of the Future in Dental Materials
The Johns Hopkins University
Baltimore, MD
J. A. Tesk
January 1984

A Technique for Characterizing the Castability of Dental Alloys
Northwestern University
Chicago, IL
J. A. Tesk
February 1984

The Positive Impact of Investment in R&D for the Dental Industry at the University Level, the Government Level and the Corporate Level
Dental Manufacturers of America
Hyannis, MA
J. A. Tesk
July 1984

CP/MAS: Resolution/Quantitative Aspects. Role of Spin Diffusion
ACS, Workshop on High Resolution NMR of Polymers in the Solid State
Williamsburg, VA
D. L. VanderHart
October 1983

Application of HR Techniques to Polymer Compatibility and Morphology
ACS, Workshop on High Resolution NMR of Polymers in the Solid State
Williamsburg, VA
D. L. VanderHart
October 1983

Carbon-13 and Proton NMR in Polymers
U. S. Naval Academy
Annapolis, MD
D. L. VanderHart
November 1983

Recent Developments in the Characterization of PET Fibers Using Solid-State NMR
Firestone Tire & Rubber Co.
Akron, OH
D. L. VanderHart
January 1984

Morphological Characterization of Polymers Using Proton and ^{13}C Solid-State NMR Techniques
Kodak Research Laboratory
Rochester, NY
D. L. VanderHart
January 1984

Characterization of Microstructure by Solid State NMR
Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy
Atlantic City, NJ
D. L. VanderHart
March 1984

Solid State ^{13}C NMR Spectra of Celluloses
Gordon Conference on Chemical Materials and Renewable Resources
Wolfboro, NH
D. L. VanderHart
July 1984

Examination of Poly (ethylene terephthalate) Fiber Morphology Using Pulse Proton NMR
26th Rocky Mountain Conference
Denver, CO
D. L. VanderHart
August 1984

High Strength Composites
Department of the Air Force
Dayton, OH
D. L. VanderHart
September 1984

Simulation Studies of Polymer Chain Dynamics
Dartmouth College
Hanover, NH
P. H. Verdier
July 1984

Aspects of the Characterization of Ultra-High Molecular Weight Polyethylene
American Chemical Society
St. Louis, MO
H. L. Wagner
April 1984

SANS Study of Delamination in Composites
Gordon Research Conference on Composites
Santa Barbara, CA
W. L. Wu
January 1984

In Vivo Wear Mechanisms of Dental Composite Resins
Academy of Dental Materials, Northwestern University
Chicago, IL
W. L. Wu
February 1984

Networks in Epoxies
Centre de Recherches sur les Macromolecules
Strasbourg, France
W. L. Wu
September 1984

Seminars for Staff and Guests

Rutherford Backscattering Studies of Diffusion in Polymers
Prof. E. J. Kramer
Cornell University
Ithaca, NY
October 1983

Quantitative DSC and Its Application to Glasses
Dr. M. J. Richardson
National Physical Laboratory
Teddington, Middlesex, UK
October 1983

Equilibrium Melting Temperature of Polyamides
Professor S. Fakirov
University of Sofia, Bulgaria
October 1983

Electrically Conductive Hybrid Polymers
Professor Gary Wnek
MIT, Cambridge, MA
October 1983

Fundamental Mechanisms Behind Relaxations in Polymers
Dr. K. L. Ngai
Naval Research Lab.
Washington, DC
October 1983

Isothermal Growth of Low Molecular Weight Polyethylene
Single Crystals from Solution
Professor R. St. John Manley
McGill University, Montreal, Canada
October 1983

Dynamic Light Scattering of Polymer Solutions
Professor N. Norio
Kyoto University, Kyoto, Japan
October 1983

Entanglement Concepts and the Deformation of Polyethylene
(Routes to High Strength Polyethylene Fibers)
Dr. Paul Smith
DuPont Co., Wilmington, DE
October 1983

Ultra Drawing of Polyethylene and Polypropylene Films Produced by Gelation-Crystallization from Solution
Professor R. St. John Manley
McGill University, Montreal, Canada
October 1983

FTIR Studies of Ionomers
Dr. Paul G. Painter
National Science Foundation
Washington, DC
October 1983

The Prediction of Creep and Recovery of Raw Rubber from Stress Relaxation Measurements
Dr. K. Fuller
Malaysian Rubber Producer's Res. Assn.
Brickedenbury, England
November 1983

Organosiloxane Segmented Copolymers
Professor J. E. McGrath
VA Polytechnic Inst. & State Univ.
Blacksburg, VA
November 1983

Biological Dielectrophoresis
Dr. H. Pohl
Oklahoma State University
Stillwater, OK 74078
November 1983

Applications of PVDF
Dr. H. R. Gallantree
Marconi Research Center
Essex, England
November 1983

Group Transfer Polymerization and Its Applications
Dr. D. Y. Sogah
DuPont, Wilmington, DE
November 1983

Structure Property Relationship in Polyester and Fibers
Professor D. S. Varma
Indian Inst. of Technology
New Delhi, India
November 1983

Polymer Self Diffusion by Forced Rayleigh Scattering
Professor H. Yu
University of Wisconsin
Madison, WI
December 1983

Solution Configurations of DNA
Dr. Carol B. Post
Harvard University
Cambridge, MA
December 1983

Phase Relations in Multicomponent Polymer Systems
Professor H. J. Roe
University of Cincinnati
Cincinnati, OH
January 1984

Studies of Ultra Orientation for Flexible Chain Thermoplastics
Professor R. S. Porter
University of Massachusetts
Amherst, MA
January 1984

Effects of Polymer Connectivity on Interfacial Properties
Dr. Y. Fabin
UCLA, Los Angeles, CA
February 1984

Dual Phase Continuity of Interpenetrating Polymer Networks
Dr. Les Sperling
Lehigh University
Bethlehem, PA
March 1984

Polymer Interfaces and Interphases
Professor J. T. Koberstein
Princeton University
Princeton, NJ
March 1984

Soliton Model of Dielectric Relaxation in Crystalline Polymers
Ms. Karna Wahlstrand
TRW-Space & Tech. Group
Redondo Beach, CA
March 1984

Synthesis of Polymers with Functionalized End Groups Via
Anionic Polymerization
Dr. Rod Quirk
University of Akron
Akron, OH
March 1984

Theory of Polymer Alloys
Professor J. Noolandi
Xerox of Canada
Mississauga, Ontario, Canada
March 1984

Liquid Crystalline Textures of Binary and Ternary Block Copolymer - Solvent(s) Systems
Dr. B. Lotz
Centre de Recherches sur les Macromolecules
Strasbourg, France
April 1984

Measurement of the Density of Polyethylene by Ultrasonics
Dr. Luc Piche
National Research Council
Montreal, Quebec, Canada
April 1984

Ferroelectricity in Vinylidene Fluoride - Trifluoroethylene Copolymers
Professor N. Koizumi
Inst. for Chemical Research
Kyoto University, Kyoto, Japan
April 1984

New Developments in Cements with Special Reference to Polyelectrolyte Materials
Dr. Dennis Smith
University of Toronto
Toronto, Canada
April 1984

New Results in Heat Capacities of Macromolecules
Dr. B. Wunderlich
Renselaer Polytechnic Inst.
Troy, NY
May 1984

Polymer Solutions: Permeation Through Pores, Photochromic Monolayers, Interaction with Solid Surfaces
Professor F. C. Rondelez
Exxon Research & Eng.
Annandale, NJ
May 1984

Thermodynamics and Morphology of Isotactic Polystyrene Physical Gels
Dr. J. M. Guenet
Centre de Recherches sur les Macromolecules
Strasbourg, France
May 1984

Microstructural Studies of Liquid Crystalline Polymers
Dr. A. M. Donald
Cavendish Laboratory
Cambridge, England
June 1984

Theory of Some Phase Transitions in Crystalline Polymers
Dr. Philip Taylor
Case Western Reserve University
Cleveland, OH
June 1984

Polymer Collapse in Bad Solvents
Dr. G. Allegra
Polytech. of Milano
Milano, Italy
July 1984

Randomly Branched Polymers
Dr. M. Daoud
Centre National de la Recherche
Scientifique
Saclay, Cedex, France
July 1984

Interaction Between Adsorbed Polymer Layers
Dr. S. Scheutjens
Laboratory for Physical & Colloid Chemistry
Agricultural University
Wageningen, The Netherlands
July 1984

Mechanics of Fracture for Composites and Adhesive Joints
Dr. S. S. Wang
Dept. of Theoretical & Applied Mechanics, University of Illinois
Urbana, IL
July 1984

Random Space Filling Cellular Structures (Sintering, Froth, and Foams)
Professor N. Rivier
Center for Nonlinear Studies, Los Alamos National Lab.
Los Alamos, NM
July 1984

In-Situ Fracture Studies of Composite Materials in SEM
Professor W. L. Bradley
Texas A&M University
College Station, TX
August 1984

Ferroelectric Phase Transition of VDF/TrFE Copolymers and Its Related Problems
Professor A. Odajima
Kokkaido University, Sapporo, Japan
August 1984

Computer Simulation of Polymer Dynamics
Professor J. Kovac
University of Tennessee
Knoxville, TN
August 1984

Relaxations in Crystalline Polymers
Professor R. Boyd
University of Utah
Salt Lake City, UT
August 1984

Fatigue of Polymer Fibers
Professor J. W. S. Hearle
University of Manchester
Manchester, United Kingdom
August 1984

A Small Angle X-ray Study of the Melting and Crystallization of Linear and Branched Polyethylene
Professor C. G. Vonk
Dept. of Physical Chemistry
DSM Central Laboratory
The Netherlands
September 1984

Technical and Professional Committee Participation and Leadership

Academy of Operative Dentistry
N. W. Rupp, Councilor,
Chairman, Glossary Committee

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

American Association for Dental Research/
International Association for Dental Research

R. L. Bowen,
Teller, 1984-85-86

L. C. Chow
Member, Mineralized Tissue Group
Member, Nominating Committee

W. G. deRijk,
Member, Student Research Committee

J. A. Tesk,
Group Representative, Executive Committee

W. E. Brown,
Member, Biological Mineralization Research Award Committee
Councilor, Mineralized Tissue Group

W. L. Wu
Member, Dental Materials Group

American Association of Dental Research - Washington Section
J. A. Tesk
Vice President

American Chemical Society
G. M. Brauer
Member, Meetings and Expositions Committee
Councilor

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

W. E. Brown
Member, Biomedical Research Support Grant Committee

W. G. deRijk
Member, Specifications Committee
Subcommittee on Waxes (Specifications 4 and 24)

American Institute of Mining, Metallurgical & Petroleum Engineering
R. M. Waterstrat
Member, Committee on Alloy Phases

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

G. M. Brauer
Government Representative
Chairman, Subcommittee on Denture Resins
Member, ZOE-Type Materials
Member, Subcommittee of Color Stability Tests

N. W. Rupp
Chairman, Alloy for Dental Amalgams
Chairman, Dispensers for Alloys and Mercury
Chairman, Mercury for Dental Amalgams
Chairman, Dental Amalgamators
Member, Pit & Fissures Committee

J. A. Tesk
Chairman, Dental Materials, Instruments and Equipment
Member, Base Metal Alloys
Secretary, Dental Implants
Member, Porcelain/Alloy Systems Committee
Chairman, USA TAG for ISO TC 106

American National Standards Institute (ANSI)
J. A Tesk
Medical Devices Standards Management Board, Exec. Committee

American Physical Society
    I. C. Sanchez
    Fellow: Division of High Polymer Physics, Chairman, 1983-84.
    Chairman of Selection Committee, APS High Polymer Physics Prize, 1983-84.

    G. B. McKenna
    Member: Publications Committee

American Society of Mechanical Engineers
    R. W. Penn
    Member, Reinforced Thermoset Plastic Corrosion Resistant Equipment

American Society for Testing and Materials
    Committe on Research & Technical Planning
    E. Passaglia
    Member: Subcommittee on Research Chairman

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

    D-11 Rubber and Rubber--Like Materials
    G. B. McKenna
    Member

    E. A. Kearsley
    Member

    D-20: Plastics
    J. H. Flynn
    Member: D20.30: Thermal Properties
        30.7 Fundamental Thermal Methods, Chairman
        30.3 Combustion Characteristics, Member
    H. L. Wagner
    Member: D20:70.05: Molecular Weight Parameters, Section Chairman
        D20:70.02: Task Force on Size Exclusion Chromatography

    D-30: High Modulus Fibers and Their Composites
        D. L. Hunston
        Member

    E-9 Fatigue
        G. B. McKenna
        Member

E-37: Thermal Measurements
J. H. Flynn
Member: E37.03: Nomenclature and Definitions

S. S. Chang
Member

F-4 Medical and Surgical Materials, and Devices
G. M. Brauer
Member, Executive Committee
Chairman, Polymeric Materials Section
Member, TAG/TC150

G. B. McKenna
Member

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

G. M. Brauer
Chairman, Councilors Committee
Member, Publications Committee
Member, Long Range Planning Committee
Chairman, Meetings & Special Events Committee

G. A. Senich
Member: Board of Managers
Chairman: Budget Committee
Chairman: Younger Chemist Committee

Department of Defense, Office of Under Secretary of Defense for Research and Engineering, Workshop on Composite Materials and Structures: Standardization, Qualification, and Certification
G. A. Senich,

Eighth International Conference on Thermal Analysis
J. H. Flynn
Workshop on current problems and reliability of kinetic data evaluated by thermal analysis, Chairman

Elliot W. Montroll Memorial Symposium on Mathematical Physics
R. J. Rubin, Session Chairman

Experimental NMR Conference
D. L. VanderHart, Member

Geis Foundation for Advancement of Dentistrty
G. C. Paffenbarger
President
Chairman, Award Committee for Dental Editorial
Chairman, Award Committee for Oral & Maxillofacial Surgery
Chairman, Award Committee for Periodontology

International Confederation for Thermal Analysis
J. H. Flynn
Member: Nomenclature Committee
Working Party on Symbols
Affiliate Councilor

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

International Electrotechnical Commission
TC046, Cables, Wires & Waveguides for Telecommunication Equipment
L. Z. Zapas
Member: WG.03: Measuring Methods of Polyethylene

International Standards Organization
TC106, Dental Materials and Devices

N. W. Rupp
Member, Restorative Materials
Chairman, WG.01, U. S. Delegation
Chairman, TG7, Alloys for Dental Amalgams

J. A. Tesk
Chairman, TAG
Chairman, U. S. Delegation

International Union of Pure and Applied Chemistry
J. H. Flynn
Member: 4. Macromolecular Division
4.2 Polymer Characterization and Properties
4.2.5 Working Party on Thermal Properties of Polymers

Lawrence Berkeley Laboratory
Director's Program Review Committee
D. L. VanderHart

Macromolecules
E. A. Di Marzio
Member: Editorial Advisory Board

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

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

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

National Health and Medical Research Council of Australia
G. C. Paffenbarger
Consultant

National Institutes of Health
L. C. Chow
Member, Oral Biology and Medicine Study Section

National Materials Advisory Board/National Research Council
G. A. Senich
Member: Reliability of Adhesive Bonds Under Severe Environments

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

North American Thermal Analysis Society
J. H. Flynn
International Confederation for Thermal Analysis Councilor
Member: Executive Committee

Ohio Dental Association
G. C. Paffenbarger
Member, Callahan Memorial Committee

Polymer Degradation and Stability (Journal)
J. H. Flynn
Member: Editorial Board

Polymer Physics Gordon Conference
E. A. Di Marzio, Chairman 1984

Polymers Division Editorial Committee
E. A. Di Marzio, Chairman

Polymers Gordon Conference (West)
I. C. Sanchez, Vice-Chairman & Chairman
Elect, 1985-1986

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

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

Thermochimica Acta (Journal)
J. H. Flynn
Member: Editorial Board

Third Conference on Fractals in the Physical Sciences
R. J. Rubin, Session Chairman

Thirteenth North American Thermal Analysis Conference
J. H. Flynn
Symposium Chairman
Plenary Lecturer

US/Yugoslav Science and Technology Program
Thermal Degradation of Polymers
J. H. Flynn, Monitor

Virginia Polytechnic Institute and State University, Center for Adhesion
D. L. Hunston
Member of External Advisory Board

Publications

Antonucci, J. M.; Venz, S.; Stansbury, J. W.; Dudderar, D. J. Low surface energy dental composites from a polyfluorinated prepolymer multifunctional methacrylate. Proc. of the 1st Annual Medical Plastic Conference of the Society of the Plastics Industry, Inc., New Brunswick, NJ, October 1983.

Brauer, G. M.; Steinberger, D. R.; Stansbury, J. W. The effect of inhibitors, accelerators and acrylic monomer ingredients on the properties of bone cement. Proc. 1st Medical Plastics Conference, The Society of Plastics Industry, Inc., New Brunswick, NJ, 1983.

Briber, R. M.; Thomas, E. L. The investigation of two crystal forms in MDI/BDO based polyurethanes. J. of Macro. Sci. Phys. 22: 509; 1983.

Brown, D. W.; Lowry, R. E.; Smith, L. E. Equilibrium acid concentrations in hydrolyzed polyesters and polyester-polyurethane elastomers. J. Appl. Poly. Sci. 28: 3779; 1983.

Chang, S. S. Heat capacity and thermodynamic properties of p-terphenyl: study of order-disorder transition by automated high-resolution adiabatic calorimetry. J. Chem. Phys. 79(12): 6229; 1983.

Chang, S. S.; Pummer, W. J.; Maurey, J. R. Fat-simulating and accelerating solvents for polyolefins and MWD of solvent extracts of polyethylenes. Polymer 24: 1267; 1983.

Chang, S. S. Specific heat of phenolic resins. ACS Polymer Preprints 24(2): 187 (1983).

Chiang, C. K. Polyacetylene as an electrode in solid state batteries. Solid State Ionics 9&10: 445; 1983.

Chiang, C. K.; Davis, G. T.; Harding, C. A; Aarons, J. Preparation and properties of polymeric solid electrolyte: polyethylene oxide-sodium iodide complexes. Solid State Ionics 9&10: 1121; 1983.

Dehl, R. E. Characterization of porosity in porous polymeric implant materials. Proc. First Annual Medical Plastics Conf., The Society of Plastics Industry, Inc., October 1983.

Dickens, B. Factor-jump thermogravimetry as applied to the study of polymer degradation, Chapter 11 in Degradation and Stabilization of Polymers. Jellinek, H. H. G. ed., Elsevier, 1983.

Dickens, B. Thermal degradation of polyisobutylene studied using factor-jump thermogravimetry. J. Thermal Anal. 27: 379; 1983.

Dickens, B.; Martin, J. W.; Waksman, D. Solar type photolytic and thermal degradation of plates of poly (methyl methacrylate), Polymer Chemistry Preprints ACS 24(2): 84; 1983.

Dickens, B.; Flynn, J. H. Thermogravimetry applied to polymer degradation kinetics, chapter 14 in ACS Advances in Chemistry Series, No. 203, Polymer Characterization: Spectroscopic Chromatographic and Physical Instrumental Methods, 219; 1983.

Fanconi, B. M. Chain scission and mechanical failure of polyethylene. J. Appl. Phys. 54: 5577; 1983.

Flynn, J. H. The isoconversional method for determination of energy approximation. Proceedings of the 12th NATAS Conf., 454; 1983.

Furukawa, T.; Lovinger, A. J.; Davis, G. T.; Broadhurst, M. G. Dielectric hysteresis and nonlinearity in a 52/48 mol% copolymer of vinylidene fluoride and trifluoroethylene. Macrmolecules 16: 1885; 1983.

Guttman, C. M.; DiMarzio, E. A. Monte Carlo modeling of kinetics of polymer crystal growth: regime III and its implications on chain morphology. J. Appl. Phys. 54(10): 5541; 1983.

Hunston, D. L.; Bascom, W. D. Effects of lay-up, temperature, and loading rate in double cantilever beam tests of interlaminar crack growth. Composite TEch. Rev. 5: 118; 1983.

Kinloch, A. J.; Shaw, S. J.; Tod, D. A.; Hunston, D. L. Deformation and fracture of a rubber-toughened epoxy: 1. microstructure and fracture studies. Polymer 24: 1341; 1983.

Kinloch, A. J.; Shaw, S. J.; Hunston, D. L. Deformation and fracture behavior of a rubber-toughened epoxy: 2. failure and criteria. Polymer 24: 1355; 1983.

Lang, S. B.; DeReggi, A. S.; Mopsik, F. I.; Broadhurst, M. G. Preexisting polarization and influence of electrode materials on PVF_2 electrets as determined by thermal pulse and pyroelectric methods. J. Appl. Phys. 54: 5598; 1983.

Lovinger, A. J.; Furukawa, T.; Davis, G. T.; Broadhurst, M. G. Crystallographic changes characterizing the curie transition in three ferroelectric copolymers of vinylidene fluoride and trifluoroethylene: 1. as crystallized samples. Polymer 24: 1225; 1983.

Lovinger, A. J.; Furukawa, T.; Davis, G. T.; Broadhurst, M. G. Crystallographic changes characterizing the curie transition in three ferroelectric copolymers of vinylidene fluoride and trifluoroethylene: 2. oriented or poled samples. Polymer 24: 1233; 1983.

Lovinger, A. J.; Furukawa, T.; Davis, G. T.; Broadhurst, M. G. Curie transitions in copolymers of vinylidene fluoride. Ferroelectrics 50: 227; 1983.

McKenna, G. B.; Kovacs, A. J. Anomalies in the physical ageing behavior of PMMA. Polymer Preprints, 24: 100; 1983.

McKenna, G. B.; Kovacs, A. J. Anomalies in the physical ageing behavior of PMMA. Proc. of the twelvth North American Thermal Analysis Society Conference, Williamsburg, VA, p. 54; 1983.

McKenna, G. B.; Zapas, L. J. Experiments on the small strain behavior of crosslinked natural rubber: 1. torsion. Polymer 24: 1495; 1983.

McKenna, G. B.; Zapas, L. J. Experiments on the small strain behavior of crosslinked natural rubber: 2. extension and compression. Polymer 24: 1502; 1983.

Peterlin, A. Decay of the spin-echo in a pulsed magnetic field gradient NMR. Makromol. Chemie 184: 2377; 1983.

Phillips, J. C.; Peterlin, A. Diffusion of ethyl acetate vapor in strained low density polyethylene. Poly. Eng. Sci. 13: 734; 1983.

Phillips, J. C.; Peterlin, A.; Waters, P. F. Stress relaxation of polyvinylidene fluoride in ethyl acetate vapor. ACS Polymer Preprints, 1983.

Phillips, J. C.; Peterlin, A.; Waters, P. F. The effect of elastic and plastic deformation on the solubility of ethyl acetate vapor in polyvinylidene fluoride (PVF_2). ACS Polymer Preprints, 1983.

Rupp, N. W. Status report on amalgamators, CDMIE, J. Am. Dent. Assn. 107: 40: 1983.

Wang, F. W.; McCrackin, F. L. Analysis of ultracentrifugation interference patterns with image digitizer: application to molecular weight determination of SRM 1478 polystyrene. Polymer 24: 1541; 1983.

Waterstrat, R. M.; Giessen, B. C. Alloy chemical comparison of the refractory metal-noble metal phase diagram T_5-T_{10} (T_5=V, Nb, Ta; T_{10} = Pd, Pt), In Alloy Phase Diagrams, Bennett, L. H.; Massalski, T. B.; Giessen, B. C. eds. New York: Elsevier, 1983.

Waterstrat, R. M.; Lachal, B.; Junod, A.; Peliggone, M.; Muller, J. Electronic specific heat and magnetic susceptibility of Ti_3P-type compounds, J. Low Temp. Physics 52(1/2): 55; 1983.

Wignall, G. D.; Wu, W. A SANS investigation into the role of melting and recrystallization during solid state deformation of polyethylene. Polymer 24(12): 354; 1983.

Wu, W. L.; Fanconi, B. M. Post-curing of dental restorative resin. Poly. Eng. Sci. 23(13): 704; 1983.

Amis, E. J.; Han, C. C.; Matsushita, Y.; Dynamic light scattering measurements of polystyrene in semidilute theta solutions. Polymer 25: 650; 1984.

Atalla, R. H.; VanderHart, D. L. Native cellulose: a composite of two different crystalline forms. Science 223: 283; 1984.

Bascom, W. D.; Bullman, G. W.; Hunston, D. L.; Jensen, R. M. The width tapered DCB for interlaminar fracture testing. Proc. of the 29th Natl. SAMPE Symp. and Exhibition, April 1984.

Bowen, R. L.; Cobb, E. N.; Misra, D. N. Adhesive bonding by surface initiation of polymerization. Ind. Eng. Chem. Prod. Res. Dev. 23(1): 78; 1984.

Brauer, G. M.; Stansbury, J. W. Cements containing syringic acid esters-o-ethoxybenzoic acid and zinc oxide. J. Dent. Res. 63: 137; 1984.

Brown, W. E.; Mathew, M.; Chow, L. C. Roles of octacalcium phosphate in surface chemistry of apatites in Adsorption on and Surface Chemistry of Hydroxyapatite, Misra, D. N. ed. Plenum, NY; 1984.

Bur, A. J.; Roth, S. C. Development of a temperature compensated PVDF transducer for dynamic pressure measurements, Annual Report of Conf. on Electrical Insulation and Dielectric Phenomena, 1984.

Bur, A. J.; Roth, S. C. Development of a polymer pressure gage with temperature compensation. Nat. Bur. Stand. (U.S.) NBSIR 84-2862, April 1984.

Chang, S. S. Migration of low molecular weight components from polymers: 1. methodology and diffusion of straight chain octadecane in polyolefins. Polymer 25: 209; 1984.

Chang, S. S. Thermodynamic Properties and Glass Transition of Polystyrene. J. Polym. Sci., Polym. Symp. 71: 59; 1984.

Chiang, C. K.; Blubaugh, E. A.; Yap, W. T. Electrochemical studies on doping of polyacetylene. Polymer 25: 1112; 1984.

Chow, L. C.; Brown, W. E.; A physicochemical bench-scale caries model. J. Dent. Res. 63: 868; 1984.

Crissman, J. M.; McKenna, G. B. Information on polymeric materials used in orthopedic devices. Nat. Bur. Stand. (U.S.) NBSIR 84-2820; January 1984.

Crissman, J. M. Mechanical behavior of ultra high molecular weight polyethylene. Nat. Bur. Stand. (U.S.) NBSIR 84-2808; January 1984.

Davis, G. T.; Chiang, C. K. High ionic conduction in polymers in high conducting polymeric materials. Sasabe, H. ed. Chemical Marketing Center, Tokyo, 1984.

Davis, G. T.; Broadhurst, M. G.; Lovinger, A. J.; Furukawa, T. Hysteresis in copolymers of vinylidene fluoride and trifluoroethylene. Ferroelectrics 57: 73; 1984.

Dehl, R. E. Characterization of porosity in porous polymeric implant materials. Trans. Second World Congress on Biomaterials; April 1984.

Dehl, R. E. Reply to "comments on 'on the characterization of porosity in PTFE-C composite implant materials by mercury porosimetry'". J. Biomed. Mater. Res. 18(1): 124; 1984.

Dickens, B.; Martin, J. W.; Waksman, D. Thermal and photolytic degradation of plates of poly (methyl methacrylate) containing monomer. Polymer 25: 706; 1984.

Dickens, B.; Marshal, J. Oxidation of polystyrene in solution. Polymer Degrad. Stab. 6: 211; 1984.

Di Marzio, E. A. A simple explanation of the polymer collapse transition: the 6/5 ths and the 2/3 rds laws. Macromolecules 17: 969; 1984.

Fanconi, B. M. Fourier transform infrared spectroscopy of polymers-theory and application. J. Test. & Eval. 12: 33; 1984.

Fanconi, B. M.; Fordyce, P.; DeVries, K. L. Chain scission and mechanical degradation of polystyrene. Poly. Eng. & Sci. 24: 421; 1984.

Flynn, J. H. Differential techniques of kinetic analyses of DSC data for thermal and photo polymerization reactions. Proceedings of 13th NATAS Conf., October 1984.

Flynn, J. H.; Florin, R. E. Degradation and pyrolysis mechanisms, chapter 14 in Pyrolysis and Gas Chromatography in Polymer Analysis, Marcel Dekker New York; 1984.

Hammouda, B.; Akcasu, A. Z.; Lodge, T. P.; Han, C. C. Dynamic scattering from bimodal polymer solutions. I. apparent diffusion coefficient. Macromolecules 17: 759; 1984.

Hinman, R. W.; Tesk, J. A. Base metal alloys in restorative dentistry. Paper 281-294, in Advanced Restorative Dentistry, 2nd ed. Baum, L.; McCoy, R. B. eds. W. B. Saunders Company, Philadephia, PA, 1984.

Hunston, D. L.; Wang, S. S.; Kinloch, A. J. Characterization of fracture behavior of adhesive joints, in Adhesive Joints: Their Formation, Characterization and Testing. Mittal, K. ed. Plenum Publishing Corp., New York, 1984.

Hunston, D. L.; Yu, C.; Bullman, G. W. Mechanical properties of compliant coating materials, in Laminar-Turbulent Boundary Layers. Uran, E. M.; Weber, H. E. eds. The American Society of Mechanical Engineers, New York, 1984.

Hunston, D. L. Viscoelastic fracture behavior for different rubber-modified epoxy adhesive formulations. Proc. of the Intl. Adhesion Conf. The Plastics and Rubber Institute, London, 1984.

Hunston, D. L. Toughening of polymers for improved composite and adhesives. Polymer Preprints 33(1): 17; 1984.

Hunston, D. L.; Bullman, G. W. Relationship between mechanical properties and performance of ink as the basis for quality control techniques. Nat. Bur. Stand. (U.S.) NBSIR 84-2901; 1984.

Kranbuehl, D. E.; Verdier, P. H. Simulation of the dynamic and equilibrium properties of many-chain polymer systems. Macromolecules 17: 749; 1984.

McCrackin, F. L.; Guttman, C. M.; Akcasu, A. Z. Monte Carlo calculations of the hydrodynamic radii of polymers in θ and good solvents. Macromolecules 17(4): 604; 1984.

Miller, J. A.; Cooper, S. L.; Han, C. C.; Pruckmayr, G. SANS from a polyurethane block copolymer. Macromolecules 17: 1063; 1984.

Misra, D. N. ed. Adsorption on and Surface Chemistry of Hydroxyapatite, Plenum Publ. Corp., New York, 1984.

Misra, D. N. Absorption of N,N-dimethyl-p-aminophenylacetic acid on hydroxyapatite, in Adsorption on and Surface Chemistry of Hydroxyapatite, Misra, D. N., ed. Plenum, New York, 1984.

Mopsik, F. I.; DeReggi, A. S. Poling behavior of polyvinylidene fluoride at room temperture. J. Appl. Phys. 44: 65; 1984.

Mopsik, F. I. Precision time-domain dielectric spectrometer. Rev. Sci. Instrum. 55: 79; 1984.

Rubin, R. J. Random-walk model of chain polymer adsorption. Behavior of critical energy and relation to a reflecting boundary condition in Random Walks and Their Applications in the Physical and Biological Sciences, American Institute of Physics Conf. Proc. Shlesinger, M. F.; West, B. J. eds. pp. 83, No. 109, 1984.

Rupp, N. W. Cements and cementation, in Advanced Restorative Dentistry, Saunders, W. B. ed., Baum and McCoy, 1984.

Sanchez, I. C. On the nature of polymer interfaces and interphases. Poly. Eng. Sci. 24: 79; 1984.

Sanchez, I. C. Corresponding states in polymer mixtures. Macromolecules 17: 967; 1984.

Sanchez, I. C. Bulk and surface thermodynamics of polymer alloys. Poly. Eng. Sci. 24: 598; 1984.

Sarkar, S. K.; Torchia, D. A.; Kopple, K. D.; VanderHart, D. L. Study of proline peptide bond conformation and ring dynamics in crystalline cyclic peptides. J. Am. Chem. Soc. 106: 3328; 1984.

Senich, G. A.; Florin, R. E. Radiation curing of coatings. J. Macromol. Sci. Revs. Macromol. Chem. Phys. C24(2): 239; 1984.

Senich, G. A.; Flynn, J. H.; Phillips, J. C.; H. Weisshaus. Cure kinetics measurements on polymer composite matrix materials. ACS Polymer Preprints 25(2): 1984.

Smith, L. E. Hydrolysis of crosslinked polyester polyurethanes. Poly. Mat. Sci. Eng. 51: 155; 1984.

Smith, L. E.; Broadhurst, M. G.; Davis, G. T.; Wang, F. W.; Fanconi, B. F.; Tesk, J. A.; Sanchez, I. C. Polymer Science and Standards Division annual report 1983. Nat. Bur. Stand. (U.S.) NBSIR 84-2813, March 1984.

Takagi, S.; Chow, L. C.; Brown, W. E.; Dobbyn, R. C.; Kuriyama, M. Parallel beam microoraliography of dental hard tissue using synchrotron radiation and x-ray image magnification, Nucl. Instr. Meth. 222(1): 1984.

Tesk, J. A.; Brauer, G. M.; Antonucci, J. M.; Wu, W. L.; McKinney, J. E.; Stansbury, J. W. Properties and Interactions of Oral Structures and Restorative Materials. Nat. Bur. Stand. (U.S.) NBSIR 84-2843; June 1984.

VanderHart, D. L.; Atalla, R. H. Studies of microstructure in native celluloses using solid-state ^{13}C NMR. Macromolecules 1984.

Wang, F. W.; Lowry, R. E.; Grant, W. H. Novel excimer fluorescence method for monitoring polymerization. 1. Polymerization of methyl methacrylate. Polymer 25: 690; 1984.

Wu, W.; Debelius, E. D.; Moffa, J. F.; Ellison, J. A. Subsurface damage layer of in-vivo worn dental composite restorations, J. Dent. Res. 63(15): 675; 1984.

Yang, H.; Shibayama, M.; Stein, R.; Han, C. C. Neutron cloud points and concentration fluctuations of polymer blends. Poly. Bull. 12: 7; 1984.

Zapas, L. J.; Crissman, J. M. The necking of semicrystalline polymers in tension, Chapter in Orienting Polymers, Ericksen, J. L. ed. Springer-Verlag; 1984.

Zapas, L. J.; Crissman, J. M. Creep and recovery behavior of ultra-high molecular weight, polyethylene in the region of small deformations. Polymer 25: 57; 1984.

Akcasu, A. Z.; Guttman, C. M. Remarks on the translational diffusion coefficient of relatively short chains. Macromolecules; in press.

Benoit, H.; Wu, W.; Benmouna, M.; Mozer, B.; Bauer, B.; Lapp, A.; Elastic coherent scattering from multi-component systems. Macromolecules; in press.

Bowen, R. L.; Eick, J. D.; Henderson, D.; Anderson, D. W. Smear layer: removal and bonding considerations. J. Op. Dent.; in press.

Brauer, G. M.; Stansbury, J. W. Intermediate restoratives from n-hexyl vanillate-eba-zno-glass composites. J. Dent. Res.; in press.

Brauer, G. M.; Antonucci, J. M. Dental applications (of polymers) in Encyclopedia of Polymer Science and Engineering, Wiley Interscience, NY; in press.

Briber, B. M.; Thomas, E. L. The crystallization behavior of random block copolymers of polybutylene terephthalate and polytetramethylene ether glycol. Polymer; in press.

Broadhurst, M. G.; Di Marzio, E. A.; Passaglia, E.; Sanchez, I. C. High polymer physics. Physics Today; in press.

Broadhurst, M. G.; Davis, G. T. Physical basis for piezoelectricity in PVDF. Ferroelectrics; in press.

Brown, D. W.; Lowry, R. E.; Smith, L. E. Hydrolysis of cross-linked polyester polyurethanes. Polymeric Material Science and Engineering Proceedings; in press.

Bur, A. J.; Roth, S. C. Measurement of a piezoelectric d constant for polyvinylidene fluoride transducers using pressure pulses, J. Appl. Phys.; in press.

Chang, S. S.; Maurey, J. M. Solubilities of BHT. J. Chem. Eng. Data; in press.

Chang, S. S.; Maurey, J. M. Migration of low molecular weight components from polymers. IV. migration of styrene monomer from polystyrene. Polymer; in press.

Chow, L. C.; Beaudreau, G. M.; Brown, W. E. Enamel fluoride profile construction from biopsy data, Caries Res.; in press.

DeCandia, F.; Perullo, A.; Victoria, V.; Peterlin, A. Mechanical and transport properties of drawn isotactic polypropylene. J. Poly. Sci. Poly. Phys. Ed.; in press.

Dehl, R. E. Characterization of porosity in porous polymer implant materials. Nat. Bur. Stand. (U.S.) NBSIR; in press.

Di Marzio, E. A.; Field theory, curdling, limit cycles and cellular automata, Proc. of Fractals Conference; in press.

Di Marzio, E. A. The nature of the glass transition. Proc. of Workshop on Glasses; in press.

Fanconi, B. M.; Sarazin, D.; McCrackin, F. L. Infrared bandshapes of methylene-d_2 bending vibrations in N-$C_{36}H_{74}$, N-$C_{36}D_{74}$ mixtures. Polymer; in press.

Fanconi, B. M. FTIR studies of molecular organization in polyethylene. Polymer Preprints; in press.

Gaylord, R. J.; Di Marzio, E. A. Viscoelastic relaxation of cross-linked polymer networks. Polymer Bulletin; in press.

Guttman, C. M. Monte Carlo Studies of two measures of polymer chain size as a function of temperature. Journal of Stat. Physics; in press.

Hasegawa, H.; Hashimoto, T.; Han, C. C. SANS and SAXS studies on molecular conformation of a block polymer in microdomain space. Macromolecules; in press.

Havens, J. R.; VanderHart, D. L. Multiple pulse proton NMR of pressure-crystallized linear polyethylene. J. Magn. Res.; in press.

Hinman, R. W.; Tetsk, J. A.; Parry, E. E.; Eden, G. T. Fit of multiple unit fixed partial denture castings. J. Prosthetic Dent.; in press.

Howell, B. F.; McCrackin, F. L.; Wang, F. W. Diffusion coefficient determination of butylated hydroxyanisole in low density polyethylene by fluorescence measurements. Polymeric Materials Science and Engineering Proceedings; in press.

Howell, B. F.; McCrackin, F. L.; Wang, F. W. Fluorescence measurement of the diffusion coefficient for butylated hydroxyanisole in low density polyethylene. Polymer; in press.

Hunston, D. L. Characterization of interlaminar crack growth in composites with the double cantilever beam specimen. Proc. Nasa Workshop on Tough Composites; in press.

Hunston, D. L.; Bascom, W. D. Failure behavior of rubber-toughened epoxies in bulk, adhesive, and composite geometries. ACS Symp. Ser.; in press.

Hunston, D. L. Composite interlaminar fracture: effect of matrix fracture energy. Composite Tech. Rev.; in press.

Kase, H. R.; Case, E. D.; Tesk, J. A. Elastic constants of two dental porcelains, J. Matls. Sci.; in press.

Kase, H. R.; Tsk, J. A.; Case, E. D. Thermal expansion of U.S. and Australian synroc B. Nuclear Tech.; in press.

Klotz, I. M.; Hunston, D. L. Mathematical models for ligand-receptor binding: real sites, ghost sites. J. Biol. Chem., in press.

Leung, P. S.; Goddard, E. D.; Han, C. C.; Glinka, C. J.; Small angle neutron scattering study of polycation and anionic surfactant complexes, J. Coll. Inter. Sci.; in press.

Martin, J. W.; Dickens, B.; Waksman, D.; Bentz, D. P.; Lechner, J. A. A preliminary stochastic model for service life prediction of a photolytically and thermally degraded polymeric cover plate material. Proc. of the 3rd World Symp. on the Durability of Building Materials, Helsinki, Finland, August 1984; in press.

Martin, J. W.; Dickens, B.; Waksman, D.; Bentz, D. P. International Proc. from Workshop on Service Life of Solar Collector Components and Materials, Technical University of Denmark, Lyngby, Denmark, December 1983; in press.

Mathew, M.; Takagi, S.; Brown, W. E. Planar $Ca-PO_4$ sheet-type structures: calcium bromide dihydrogen phosphate tetrahydrate, $CaBr(H_2PO_4)\cdot 4H_2O$, and calcium iodide dihydrogenphosphate tetrahydrate, $CaI(H_2PO_4)\cdot 4H_2O$, Acta Cryst.; in press.

Matsushita, Y.; Noda, Y.; Nagasawa, M.; Lodge, T. P.; Amis, E. J.; Han, C. C.; Macromolecules; in press.

McKenna, G. B.; Zapas, L. J. The time dependent strain energy function for a polymeric glass. Polymer; in press.

McKenna, G. B.; Kovacs, A. J. Physical ageing of PMMA in the non-linear range: torque and normal force measurements. Poly. Eng. Sci.; in press.

McKenna, G. B. Measurement of the torque and normal force in torsion in the study of the thermoviscoelastic properties of polymer glasses, in Relaxation Effects in in Disordered Systems, K. L. Ngai, ed.; in press.

McKinney, J. E.; Wu, W. L. Chemical softening and wear. J. Dent. Res.; in press.

Peterlin, A.; deCandia, F. D.; Vittoria, V. The time dependence of the mechanical and transport properties of drawn and annealed linear polyethylene. J. Poly. Sci.; in press.

Peterlin, A. Transport properties as an extremely sensitive indication of the status of the amorphous component in the elastically and plastically deformed semicrystalline polymer. J. Poly. Sci. Poly. Phys. Ed.; in press.

Peterlin, A. Physical methods of property modification of semicrystalline polymers. Industrial Matls. Sci. & Eng.; in press.

Peterlin, A. The diffusion and permeability in a homogeneous non-ideal membrane. J. of Membrane Science; in press.

Phillips, J. C.; Peterlin, a.; Waters, P. F. The influence of strain deformation on the solubility of ethyl acetate vapor in polyvinylidene fluoride (PVF_2). J. Poly. Sci. Poly. Phys. Ed.; in press.

Prince, E.; Takagi, S.; Mathew, M.; Brown, W. E. The structure of dicalcium potassium heptahydrogen tetrakis phosphate dihydrate, $Ca_2KH_7(PO_4)_4 \cdot 2H_2O$, by x-ray and neutron diffraction, Acta Cryst.; in press.

Rubin, R. J. Transport in a disordered one-dimensional system: a fractal view. J. Stat. Phys; in press.

Sanchez, I. C. Critical properties, potential force constants, and structure of organic molecules, AICHE J.; in press.

Senich, G. A.; Flynn, J. H.; Phillips, J. C. Analysis of synthetic ink vehicles. Nat. Bur. Stand. (U.S.) NBSIR; in press.

Stansbury, J. W. Divanillates and polymerizable vanillates as ingredients of dental cements. J. Biomed. Mater. Res.; in press.

Takagi, S.; Mathew, M.; Brown, W. E. The strcture of ammonium calcium phosphate heptahydrate, $Ca(NH_4)(PO_4) \cdot 7H_2O$, Acta Cryst.; in press.

Tesk, J. A.; Waterstrat, R. M. Physical metallurgy of dental casting alloys-Co-Cr-Mo system, Ni-Cr system, ferritic and austenitic steels, titanium alloys. Article #343/00314, Encyclopedia of Materials Science and Engineering; Pergamon Press; in press.

Tung, M. S.; Brown, W. E. Effects of ionic organic material on enamel demineralization, Caries Res.; in press.

VanderHart, D. L.; Khoury, F. A. Quantitative determination of the monoclinic crystalline phase content in polyethylene by ^{13}C NMR. Polymer; in press.

Wagner, H. L., The Mark-Houwink-Sakurada equation for linear polyethylene. J. Phys. Chem. Ref. Data; in press.

Wang, F. W.; Howell, B. F. A novel fluorescence technique for measurements of additive migration from polymers. Polymer; in press.

Wu, W.; Wiswe, D.; Zachmann, H. G.; Huhn, K. A SANS study of partially segregated polyethylene terephthatale blends. Polymer; in press.

Zupancic, I.; Lahajnar, G.; Blinc, R.; Reneker, D. H.; VanderHart, D. L. NMR self diffusion study of polyethylene and paraffin melts. J. Poly. Sci. Poly. Phys. Ed.; in press.

Special Reports

Paffenbarger, G. C.; Snell, B.; Johnson, L. B. Jr.; Wawner, F. E. Jr.; Lawless, K. R. Twenty years of research in dental materials in the development of materials science at the University of Virginia. University of Virginia Report No. UVA 1523591/MS 84/101; August 1983.

External Recognition

Dr. C. C. Han
Dillon Medal, Awarded by Division of High Polymer Physics of the American Physical Society

New SRMs

SRM 871, Sulfur, G. W. Bullman and G. B. McKenna, 1983

SRM 384, N-t-butyl-benzothiazole-sulfenamide, G. W. Bullman and G. B. McKenna, 1984

Industrial Interactions

Archival Technical Papers Coauthored with Industrial Employees

Hunston, D. L.; Bascom, W. D. Effects of lay-up, temperature, and loading rate in double cantilever beam tests of interlaminar crack growth. Composite Technology Review 5: 118; 1983.

Atalla, R. H.; VanderHart, D. L. Native cellulose: a composite of two different crystalline forms. Science 233: 283; 1984.

Bascom, W. D.; Bullman, G. W.; Hunston, D. L.; Jensen, R. M. The width tapered DCB for interlaminar fracture testing. Proc. of the 29th National SAMPE Symposium and Exhibition, April 1984.

VanderHart, D. L.; Atalla, R. H. Studies of microstructure in native celluloses using solid-state ^{13}C NMR. Macromolecules 1984.

Hunston, D. L.; Bascom, W. D. Failure behavior of rubber-toughened epoxies in bulk, adhesive, and composite geometries. ACS Symposium Series; in press.

Research Associates

Alta Technology, Inc. - S. Venz

American Dental Association Health Foundation -
R. L. Blosser
R. L. Bowen
W. E. Brown
C. Carey
M. W. Chalkley
L. C. Chow
M. L. Conner
W. G. DeRijk
N. Eidelman
A. A. Giuseppetti
T. M. Gregory
K. A. Jennings
A. D. Johnston
M. Mathew
D. L. Menis
D. N. Misra
V. K. Misra
G. C. Paffenbarger
E. F. Prestemon
N. W. Rupp
C. T. Schreiber
L. E. Setz
B. A. Sieck
S. Takagi
B. B. Tomazic
M. S. Tung
G. L. Vogel
R. M. Waterstrat

ARCO Chemical Co - L. E. Bruggemen
D. A. Campbell

Bethelehem Steel - J. R. Kastelic

Brown University Research Foundation - D. DeRossi

Dentsply International, Inc. - S. Venz

Exxon Chemical Co. - D. Lohse

General Electric - C. F. Hansen

IMASS, Inc. - E. H. Frank

National Institute of Dental Research/NIH
E. A. Eanes
B. O. Fowler
A. W. Hailer

Rheology Research - E. A. Kearsley

POLYMERS DIVISION

LESLIE E. SMITH, CHIEF,
S. M. THOMAS, ADMIN. OFFICER
B. A. HYDE, SECRETARY
X3734

B. M. FANCONI, DEPUTY CHIEF
J. S. BURTON[9], Secretary

M. C. BROADHURST, ASST. CHIEF

440.01
ELECTRICAL PROPERTIES

G. T. DAVIS D[1]
Leader, x3851

A. J. BUR	D
C. K. CHIANG	D
A. S. DEREGGI	D
R. K. EBY[5]	D
S. EDELMAN[5]	B[2]
E. H. FRANK[20]	D
C. HANSEN[23]	D
C. A. HARDING	
G. R. HARRIS[4,5]	D
L. A. HOFFMASTER	
J. R. KASTELIC[11]	D
S. J. KRYDER[7]	B
R. S. MARVIN[5]	D
C. MASSOT[26]	D
F. I. MOPSIK	D
S. C. ROTH	M[8]
T. TAKAHASHI[5,19]	D
K. WAHLSTRAND[14]	D

440.02
CHEMICAL PERFORMANCE & STANDARDS

F. W. WANG D
Leader, x3321

D. W. BROWN	M
L. E. BRUGGEMAN[27]	B
D. A. CAMPBELL[27]	B
B. DICKENS	D
J. G. DILLON[4,5]	D
R. E. FLORIN[5]	D
J. H. FLYNN	D
W. H. GRANT	D
C. M. GUTTMAN	D
B. F. HOWELL	D
D. E. KRANBUEHL[6,13]	D
R. E. LOWRY	B
J. R. MAUREY	B
W. J. PUMMER	M
H. L. WAGNER	D
W. K. WILSON[5]	D
P. H. VERDIER	D

440.03
MECHANICAL PERFORMANCE

B. M. FANCONI D
Leader, x3734

M. L. BOLZ[6,7]	B
J. M. CRISSMAN	D
E. A. KEARSLEY[21]	D
F. A. KHOURY	D
J. MAZUR	D
G. B. MCKENNA	D
E. PASSAGLIA	D
A. PETERLIN[5]	D
D. L. VANDERHART	D
L. A. WOOD[5]	D
L. J. ZAPAS	D

440.04
POLYMER COMPOSITES

D. L. HUNSTON D
Leader, x3318

G. W. BULLMAN	
S. S. CHANG	D
E. A. DEBELIUS	
R. E. DEHL	D
K. FLYNN	B
A. GILAT[5]	D
J. A. HINKLEY[5,3]	D
J. T. KOBERSTEIN[5]	D
J. E. MARSHALL	
J. N. OWENS[5,28]	
J. C. PHILLIPS	D
J. C. SMITH[5]	D
R. D. STIEHLER[5]	D
W. L. WU	D

440.05
POLYMER BLENDS

I. C. Sanchez D
Leader, X3251

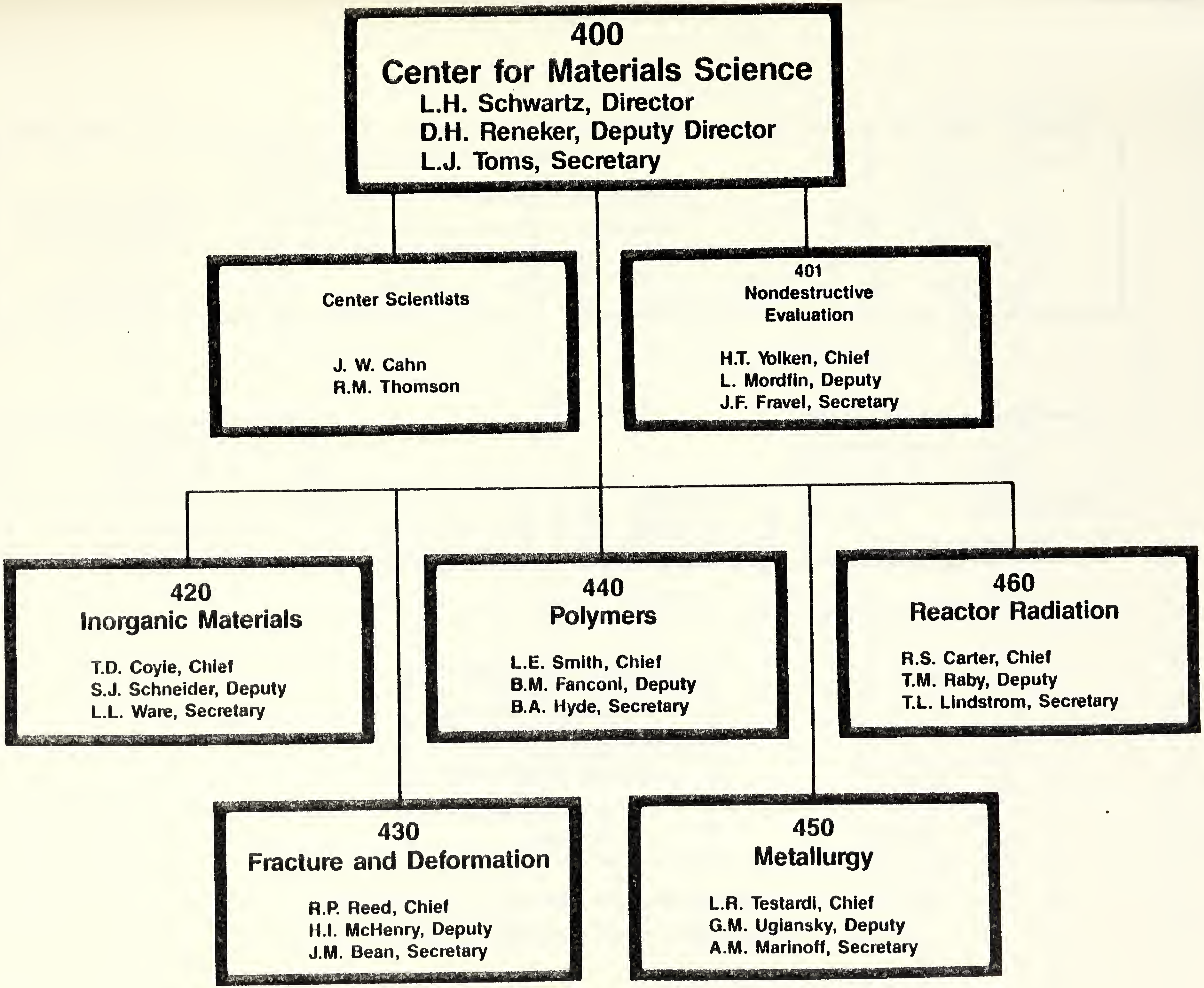
E. J. AMIS[6,24]	D
J. D. BARNES	D
B. J. BAUER	D
R. M. BRIBER[14]	D
T. CHANG[24]	D
E. A. DI MARZIO	D
C. C. HAN	D
M. LANDRY[5,24]	D
T. P. LODGE[6,24]	D
D. LOHSE[10]	D
F. L. MCCRACKIN	D
Y. MUROGA[5]	D
M. OKADA[5]	D
R. REYNOLDS	
R. J. RUBIN	D
Q. TRAN-CONG[5]	D

440.06
DENTAL & MEDICAL MATERIALS

J. A. TESK D
Leader, x3336
(ADA x3512)

J. M. ANTONUCCI	D
R. L. BLOSSER[15]	B
R. L. BOWEN[15,16]	DDS
G. M. BRAUER	D
W. E. BROWN[15]	D
C. M. CAREY[15]	M
M. W. CHALKLEY[15]	B
T. M. CHEN[5]	D
L. C. CHOW[15]	D
E. COBB[5,17]	DDS
M. L. CONNER[15]	
W. E. CRITCHLEY	
W. DERIJK[15]	D
E. A. EANES[22]	D
N. EIDELMAN[15]	D
B. O. FOWLER[22]	B
A. A. GIUSEPPETTI[15]	
T. M. GREGORY[15]	M
A. W. HAILER[22]	B
R. W. HINMAN[5,18]	DDS
K. A. JENNINGS[15]	
A. D. JOHNSTON[15]	D
J. S. KUO[5]	DDS
M. MATHEW[15]	D
J. E. MCKINNEY	B
D. L. MENIS[15]	B
D. N. MISRA[15]	D
G. C. PAFFENBARGER[15]	DDS
R. W. PENN	D
E. F. PRESTEMON[15]	
N. W. RUPP[15]	DDS
C. T. SCHREIBER[15]	B
L. E. SETZ[15]	
B. SIECK[15]	B
J. W. STANSBURY	B
S. TAKAGI[15]	D
H. S. TALWAR[22]	D
A. TATEVOSSIAN[5]	
B. B. TOMAZIC[15]	D
M. G. TUNG[15]	D
S. VENZ[25]	D
G. L. VOGEL[15]	D
R. M. WATERSTRAT[15]	D
R. P. WHITLOCK[5,18]	DMD
D. WHITMAN[5,18]	DMD

[1] "D" - PH.D.
[2] "B" - BACHELOR
[3] NASA LANGLEY
[4] FOOD & DRUG ADMIN.
[5] GUEST WORKER
[6] WHILE ACTUALLY EMPLOYED
[7] REHIRED ANNUITANT
[8] "M" - MASTERS
[9] PART TIME
[10] EXXON RES. ASSOC.
[11] BETH. STEEL RES. ASSOC.
[12] IPA - U. AKRON
[13] WILLIAM & MARY
[14] POST DOCTORAL
[15] ADA RES. ASSOC.
[16] DIRECTOR, ADA
[17] GEORGETOWN DEN. SCH.
[18] U.S. NAVY
[19] UBE INDUSTRIES, LTD.
[20] IMASS CORP. RES. ASSOC.
[21] RHEOLOGY RES. ASSOC.
[22] NIH (NIDR)
[23] GE RES. ASSOC.
[24] UNIV. OF WISCONSIN
[25] DENTSPLY RES. ASSOC.
[26] ALTA TECH. RES. ASSOC.
[27] ARCO CHEM. RES. ASSOC.
[28] PRINCETON



400
Center for Materials Science
L.H. Schwartz, Director
D.H. Reneker, Deputy Director
L.J. Toms, Secretary

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

401
Nondestructive Evaluation
H.T. Yolken, Chief
L. Mordfin, Deputy
J.F. Fravel, Secretary

420
Inorganic Materials
T.D. Coyle, Chief
S.J. Schneider, Deputy
L.L. Ware, Secretary

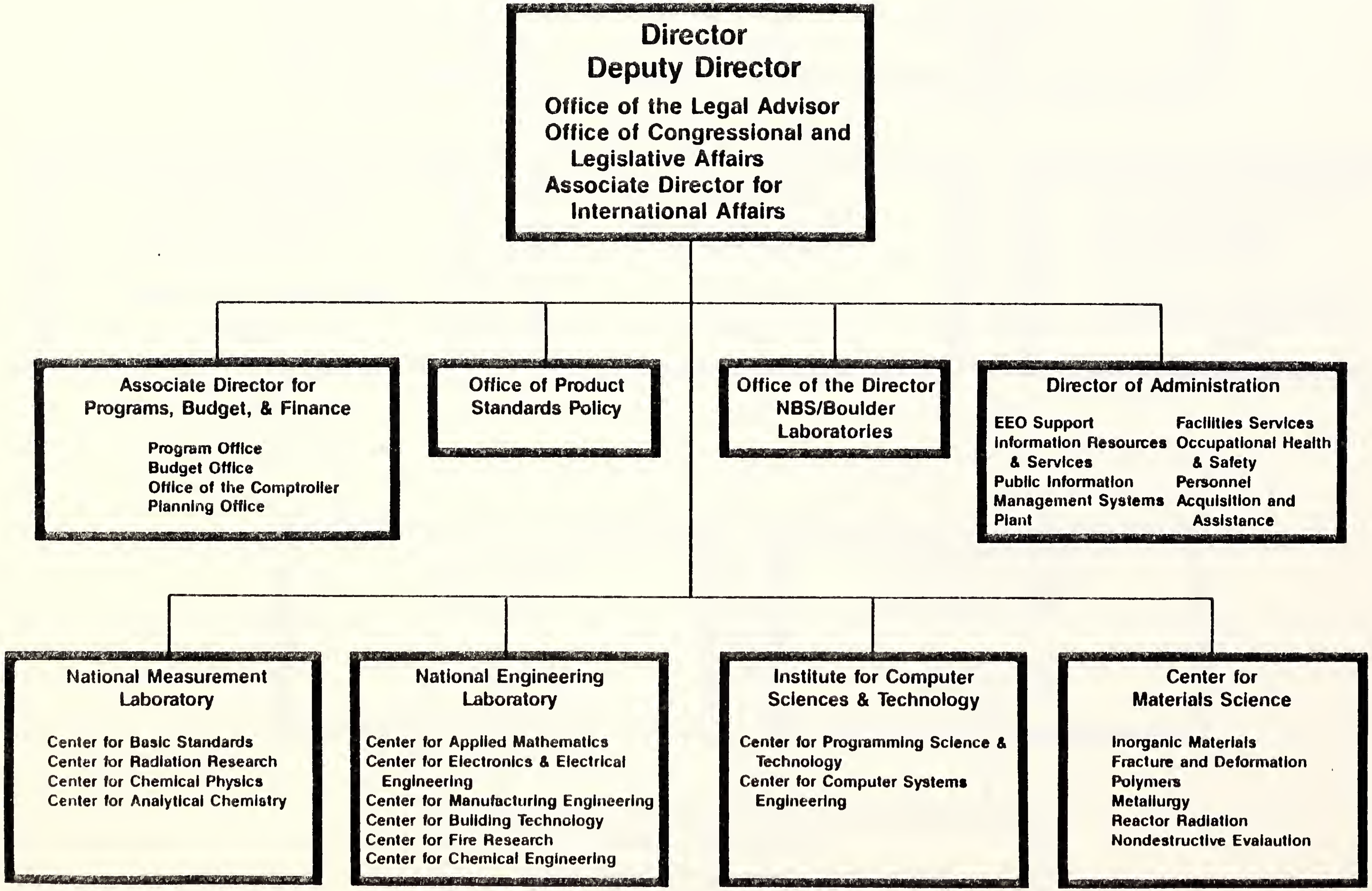
430
Fracture and Deformation
R.P. Reed, Chief
H.I. McHenry, Deputy
J.M. Bean, Secretary

440
Polymers
L.E. Smith, Chief
B.M. Fanconi, Deputy
B.A. Hyde, Secretary

450
Metallurgy
L.R. Testardi, Chief
G.M. Ugiansky, Deputy
A.M. Marinoff, Secretary

460
Reactor Radiation
R.S. Carter, Chief
T.M. Raby, Deputy
T.L. Lindstrom, Secretary

U.S. Department of Commerce
National Bureau of Standards



Director
Deputy Director
Office of the Legal Advisor
Office of Congressional and Legislative Affairs
Associate Director for International Affairs

Associate Director for Programs, Budget, & Finance
- Program Office
- Budget Office
- Office of the Comptroller
- Planning Office

Office of Product Standards Policy

Office of the Director NBS/Boulder Laboratories

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

National Measurement Laboratory
- Center for Basic Standards
- Center for Radiation Research
- Center for Chemical Physics
- Center for Analytical Chemistry

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

Institute for Computer Sciences & Technology
- Center for Programming Science & Technology
- Center for Computer Systems Engineering

Center for Materials Science
- Inorganic Materials
- Fracture and Deformation
- Polymers
- Metallurgy
- Reactor Radiation
- Nondestructive Evalaution

NBS-114A (REV. 2-80)

U.S. DEPT. OF COMM. **BIBLIOGRAPHIC DATA SHEET** *(See instructions)*	1. PUBLICATION OR REPORT NO. NBSIR 84-2946	2. Performing Organ. Report No.	3. Publication Date January 1985

4. TITLE AND SUBTITLE

POLYMERS DIVISION ANNUAL REPORT 1984

5. AUTHOR(S)

L.E. Smith, B.M. Fanconi, G.T. Davis, F.W. Wang, I. C. Sanchez, D.L.Hunston, J.A. Tesk

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

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

7. Contract/Grant No.

8. Type of Report & Period Covered
Annual Report
10/1/83 - 9/30/84

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

Center for Materials Science
National Bureau of Standards
Gaithersburg, MD 20899

10. SUPPLEMENTARY NOTES

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

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

Technical activities of the Polymers Division for FY 84 are reviewed. Included are descriptions of the 6 Tasks of the Division, project reports, publications list, and other technical activities

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

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

13. AVAILABILITY

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

14. NO. OF PRINTED PAGES
140

15. Price
$14.50