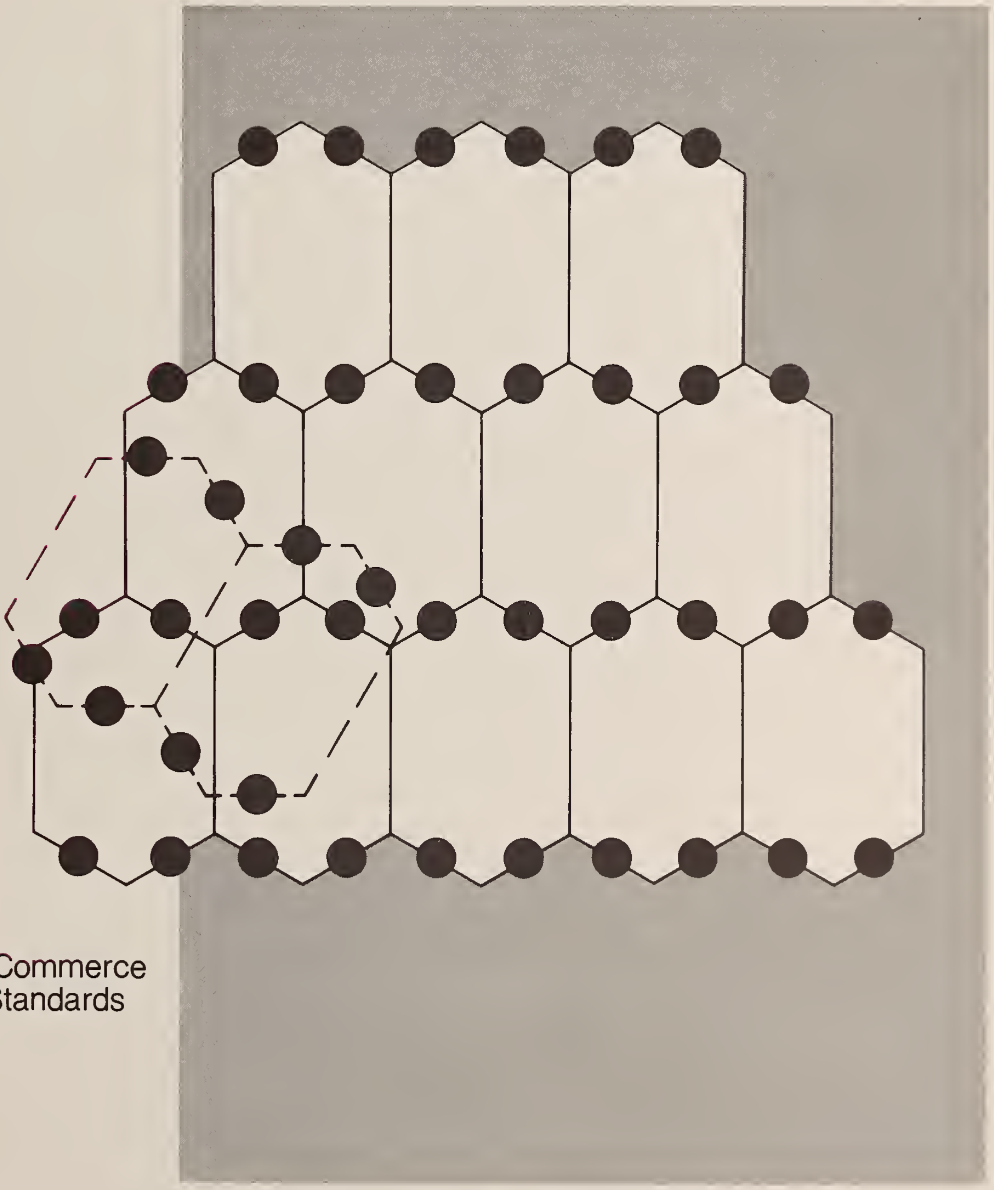
Institute for Materials Science and Engineering

POLYMERS



NBSIR 85-3190
U.S. Department of Commerce
National Bureau of Standards

Technical Activities 1985

Idealized representation of a crosslinked epoxy network. The dark circles show the portions of the molecule labeled with deuterium atoms to provide points of contrast for small angle neutron scattering. Neutron scattering experiments can provide quantitative characterization of the degree of disorder in crosslinked networks, an important factor in the mechanical performance of these polymers used as adhesives and matrix materials for advanced composites.

Institute for Materials Science and Engineering

POLYMERS

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

NBSIR 85-3190
U.S. Department of Commerce
National Bureau of Standards

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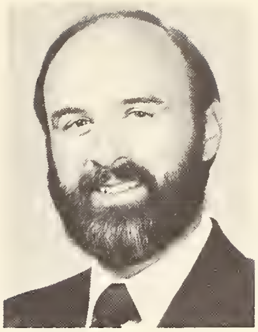
Polymers Division



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

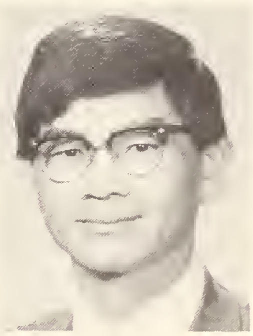
BRUNO M. FANCONI, Deputy Chief. Dr. Fanconi was born in Merced, California. He earned degrees in physical chemistry from the University of California at Los Angeles and the University of Washington. He joined the staff of NBS in 1971.

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

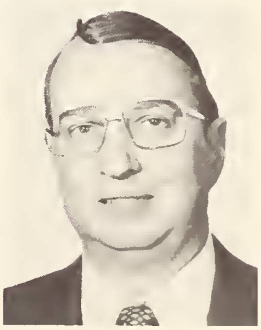
G. THOMAS DAVIS, Group Leader, Electrical Properties. Dr. Davis was born in Montour Falls, New York. He earned degrees in chemical engineering at Cornell University and physical chemistry at Princeton University. Prior to joining NBS in 1964, he worked for Esso Research and Engineering Co. and taught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

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

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



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



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

BRUNO M. FANCONI, Group Leader, Mechanical Performance.

TABLE OF CONTENTS

PAGE

INTRODUCTION

POLYMERS DIVISION

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

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

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

The Groups concerned with polymer blends and composites are responsible for all aspects of the processing and performance of these advanced materials. The formation of these Groups reflects the growing importance of blends and composites to the polymer-related industries. Polymer blends are one effective way for domestic polymer producers to respond to competitive pressure from foreign producers with access to very inexpensive feedstocks. New products can be tailored to meet specific market requirements by blending two or more polymers, without abandoning present production facilities and without the large capital expenditures necessary to produce a totally new polymer. The principal industrial need in this field is for a fundamental science base to underlie the design and processing of new blends. This includes needs for measurement methods to produce data for polymer phase diagrams, data on polymer diffusion and the kinetics of phase separation, and theoretical models that accurately describe the thermodynamics and kinetics of blends.

Although only about 10% of polymer production is now used in polymer matrix composites, the current and potential impact of these materials on other industries is dramatic. Military and aerospace uses of advanced composites are already large and diverse; major components of automobiles are beginning to be constructed of fiber-reinforced composites and many opportunities exist in the construction, machinery, and electronics markets. Two major factors have inhibited the growth of composites in mass markets: inability to process the materials inexpensively and reliably; and uncertainty about the performance of these anisotropic materials under complex loads, particularly at failure.

The Composites Group has programs aimed at solving some of the measurement and basic science aspects of these two problems. More efficient processing will come from automated manufacture aided by appropriate feedback control sensors. The identification of materials properties that can be monitored and development of measurement methods suitable for process control are major objectives of the Group with additional support from the NBS Non-Destructive Evaluation program.

Failure behavior of composites is very complex and the fundamental science of heterogeneous materials is not advanced enough to be confident of predictions based on much less than prototype testing. Much work needs to be done in this area but progress is being made in understanding the resistance to composites to interlaminar shear failure, at least under simple types of loads. Our current emphasis is on developing reliable test methods for interlaminar shear strength and trying to understand failure behavior in terms of the properties of the constituent materials.

The Dental and Medical Materials Group is a model of effective private sector-government cooperation. For over sixty years the American Dental Association (ADA) and NBS have worked together to improve dental materials and devices. Virtually all the major materials used by dentists in the United States today have been developed or influenced by this joint program. This year the NBS program achieved another dimension when Research Associates from the National Institutes of Dental Research (NIDR) joined with those from the ADA, the dental industry, and domestic and foreign guest workers to become part of what is now the most comprehensive program of its kind anywhere in the world.

Each of these programs is described in more detail in this report. For management purposes, the technical program is divided into six task areas, as follows:

POLYMER STANDARDS AND CHEMICAL PERFORMANCE

BLENDS PROCESSING

BIOMATERIALS SCIENCE, METROLOGY AND STANDARDS FOR IMPROVED DURABILITY, APPLICATIONS AND MANUFACTURING OF DENTAL AND MEDICAL MATERIALS

MECHANICAL PERFORMANCE OF POLYMERS

PROCESSING AND RELIABILITY OF POLYMER COMPOSITES

MICROSTRUCTURE AND PERFORMANCE OF DIELECTRIC PLASTICS

RESEARCH STAFF

Antonucci, Joseph M.	• Synthetic and polymer chemistry • Dental composites and cements • Antioxidants
Barnes, John D.	• Gas and vapor transport in polymers • X-ray scattering • Computer applications in polymer measurements
Bauer, Barry J.	• Polymer synthesis • Neutron, x-ray and light scattering
Blosser, Richard L.*	• Adhesion measurements
Bowen, Rafael L.*	• Adhesion • Polymer composites • Biocompatibility
Brauer, Gerhard M.	• Synthetic and polymer chemistry • Dental composites and cements • Adhesion • Orthopedic materials
Broadhurst, Martin G.	• Dielectric measurement • Piezoelectric and pyroelectric modeling and theory • Equation of state of polymers • Ionic conduction
Brown, Daniel W.	• Pyrolysis of polymers • Lifetime of polyurethanes and polyesters
Brown, Walter E.*	• Solution chemistry of calcium phosphate (CAPH) compounds, • Biological CAPH compounds, • Atherosclerotic plaque
Bur, Anthony J.	• Dielectric properties of polymers • Piezoelectric, pyroelectric polymers • Polymeric transducers
Carey, Clifton M.*	• Dental plaque • Microanalytical analysis techniques
Chang, Shu Sing	• Thermal Properties of Polymeric Materials • Electronic Packaging • Polymer Phase Transitions • Precision Electrical and Temperature Measurements

*Research Associate

Chiang, C. K.	● Electrical properties of polymeric, ceramic and organic materials ● AC electrical impedance spectroscopy
Chow, Laurence C.*	● Calcium phosphate compounds ● Dental and bioimedical cements ● Solution chemistry ● Topical dental fluorides
Crissman, John M.	● Mechanical Behavior ● Environmental Stress-Cracking ● Failure and Fracture of Polymers
Davis, G. Thomas	● Piezoelectricity in polymers ● Polymer crystallization ● X-ray diffraction of polymers
Debelius, Elizabeth E.	● Mechanical Properties of Paper ● Mechanical Testing of Composites ● Measurement of Dental Materials
Dehl, Ronald E.	● Surface Analysis ● Porosity Measurements ● Ellipsometry ● Bonding of Polymers and Composites
DeReggi, Aime S.	● Polarization-depth profiles in polymers ● Space charge in dielectrics ● Ferroelectric polymers ● Polymeric piezo- and pyroelectric devices
de Rijk, Waldemar G.*	● Clinical dentistry ● Ceramic materials ● Expansion characteristics of solids and semi-solids ● Statistical analysis
Dickens, Brian	● Kinetics of thermal degradation of polymers ● Photodegradation of poly (methyl methacrylate) ● Curing studies of thermosetting printing inks
Di Marzio, Edmund A.	● Statistical mechanics of polymers ● Phase transitions ● Glasses ● Polymers at interfaces

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Eidelman, Naomi N.*	• Atherosclerotic plaque
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Fowler, Bruce O.*	• Laser Raman structural analysis of calcium phosphates
Giuseppetti, Anthony A.*	• Casting of dental alloys • Titanium alloys
Grant, Warren H.	• Adsorption of polymers • Fluorescence measurements of polymeric systems
Gregory, Thomas M.*	• Calcium phosphate compounds • Surface chemistry
Guttman, Charles M.	• Solution properties of polymers • Diffusion of small molecules into polymeric systems • Semicrystalline polymer chain configurations • Kinetics of polymer crystal growth
Han, Charles C.	• Polymer blends • Polymer characterization • Small angle neutron scattering • Static and quasi-elastic light scattering
Hailer, Arthur W.*	• Chemical reactions, chemical analysis
Howell, Barbara F.	• Electron microscopy • Spectrophotometry • Light microscopy
Hunston, Donald L.	• Adhesion Science and Technology • Fracture Behavior of Polymers • Processing and Failure Behavior of Composites • Flow Behavior of Dilute High Polymer Solutions • Macromolecule-Small Molecule Binding

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Johnson, Allen D.*	• Nuclear magnetic resonnance • Mossbauer studies • Chemical adhesion
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Lowry, Robert E.	• Applications of fluorescence spectroscopy to polymeric systems • Synthesis of chromophore-labeled polymers
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Maurey, John R.	• Ultracentrifugation • Rayleigh light scattering • Osmometry • Densimetry • Refractometry
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Phillips, Joseph C.	• Viscosity & Normal Stress Measurements • Environmental Effects on Transport and Mechanical Properties • Curing Behavior of Thermoset Inks
Pummer, Walter J.	• Synthesis and characterization of aromatic polyimides • Synthesis of specialty compounds • Blending of radio-tracers into polymers
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Rubin, Robert J.	• Statistics of polymer chain configurations • Theory of Brownian motion • Random walk models with traps • Polymers near surfaces
Rupp, Nelson W.*	• Clinical dentistry • Amalgams • Gold foils • Dental standards • Composites • Titanium castings

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Sieck, Barbara*	● Calcium phosphate compounds ● Chemical analysis
Smith, Leslie E.	● Adsorption of polymers ● Polymer degradation reactions
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Tomazic, Branko*	● Atherosclerotic plaque ● Biological calcium phosphate compounds
Tung, Ming S.*	● Biological solution chemistry of calcium phosphate compounds ● Equilibrium studies
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Venz, Sabine*	● Clinical dentistry ● Dental composites ● Dental polymers
Verdier, Peter H.	● Polymer solution properties ● Polymer chain dynamics in solution ● Statistical analysis of data ● Error estimation ● Computer simulation of polymer chain dynamics

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Wahlstrand, K. J.	● Mathematical analysis ● Computer simulation ● X-ray pole figures
Wang, Francis W.	● Photophysics and photochemistry of polymers ● Fluorescence spectroscopy ● Thermodynamic and frictional properties of macromolecules
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POLYMERS DIVISION

November 1985

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POLYMER STANDARDS AND CHEMICAL PERFORMANCE

Task 14332

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

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

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

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

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

FY 85 Significant Accomplishments

- A series of poly(methyl methacrylate) is being produced with support from the Navy and the Office of Standard Reference Materials. These SRM's will be used for quality control of antifouling paints and as calibrating materials for the analysis of acrylic polymers. The limiting viscosity number (intrinsic viscosity) and the number-average molecular weight for the highest molecular weight polymer in the series have been determined.

- Two "linear low density" polyethylenes used in gas piping (one with, and the other without pigment) are being characterized for certification as Standard Reference Materials, with support from the Gas Research Institute and the Office of Standard Reference Materials. Such a standard would be useful not only to the gas distribution and associated industries but also to the rest of the scientific community. Preliminary experiments have established the conditions necessary for size exclusion chromatography, such as the type of columns, concentration, and temperature.

- No significant difference has been found between the diffusion coefficients of the cyclic polystyrene polymer and that of the linear polystyrene polymer when they have the same molecular weight. The diffusion coefficients of fluorophone-labelled cyclic polystyrene in dilute and semi-dilute linear polystyrene solutions were measured by a novel method called Fluorescence Recovery After Photobleaching (FRAP).

Characterization and Standards

Subtask 1 of Task 14332

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

[1]University of Maryland, Baltimore County

Work in this Subtask proceeds primarily along four lines: Production of polymer standards; critical evaluation of experimental data on polymers; development of improved methods for characterizing polymeric materials and development of fundamental concepts related to the solution properties of polymers. The linear low density polyethylene standards currently under development, which are partly supported by the Gas Research Institute, will aid in the development of polyethylene gas pipes with improved properties. The poly(methyl methacrylate) standards currently in production will aid the Navy, which is partially supporting their production, in the development of long-lived antifouling paints for ships' hulls. In addition, both kinds of standards will be generally useful in the plastics and related industries, both for equipment calibration and as materials for research. The critical evaluation of literature data on the relationships between limiting viscosity number and molecular weight for atactic polystyrenes will aid in materials characterization in this important segment of the plastics industry. Development of a self-calibrating gel permeating chromatograph should eventually result in substantial reductions in the cost of producing polymeric Standard Reference Materials, and should allow much more detailed characterization of polymeric materials than has thus far been practical. Fluorescence measurements of polymer diffusion and polymer-polymer interactions will provide data that are needed for welding of polymers, for designing polymerization reactors, and for producing molecularly reinforced composites. Finally, the theoretical studies of translational diffusion constants and chain-molecule dynamics will yield fundamental concepts that will not only guide the experimental work on polymer-solution properties but also give insight on the processibility and the end-use properties of polymeric materials.

Characterization of Gas Research Institute Polyethylene

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

The natural or unpigmented resin, designated SRM 1496, will be certified for limiting viscosity number, and a supplementary (non-certified) distribution in molecular weight. For the pigmented resin, designated SRM 1497, a certified melt flow rate and a supplementary (non-certified) molecular weight distribution will be determined. Later on the molecular weight of SRM 1496 will be measured for certification.

A thousand pound shipment of the unpigmented resin has been received and preliminary experiments have established the conditions necessary for size exclusion chromatography, such as the type of columns, concentration, and temperature. It was also found that a temperature of 160 °C for one hour is necessary for complete solution. This lot of resin has also been tested for uniformity by determining the viscosity number in trichlorobenzene at 130 °C for samples from 10 different locations in the container.

Poly(methyl methacrylate) Standard Reference Materials

A series of three poly (methyl methacrylate) Standard Reference Materials, certified for molecular weights and limiting viscosity numbers, will be produced. These standards will be used by the Navy, which is providing partial support for their production, in quality control procedures for Navy specifications for commercial antifouling paints used on ships' hulls. They will also be widely used in the plastics and related industries for the calibration of size-exclusion chromatographs used for quality control, and for research and development.

Three poly(methyl methacrylate) polymers with molecular weights of approximately 8,000, 30,000 and 120,000, which are to become SRM's 1487, 1488, and 1489, respectively, have been blended, bottled, and examined by nuclear magnetic resonance (NMR) for chemical identify and tacticity. The limiting viscosity number of SRM 1489 has been determined by capillary viscosity measurements for certification. The number average molecular weight, which is also to be certified, has been determined by membrane osmometry for this same SRM. Both types of measurements were made at 25°C in toluene.

Critical Evaluation of Mark-Houwink Relations for Atactic Polystyrene

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

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

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

where K and a are the empirically determined Mark-Houwink parameters, which depend on the specific solvent and temperature. An incomplete compilation of these data can be found in the handbooks, but a critical assessment is not yet available. Yet these data are used extensively to obtain molecular weights as well as to calibrate size exclusion chromatography columns.

Detailed examination of the literature revealed that many of the determinations of K and a were made by indirect rather than by absolute measurements of molecular weight, or by the use of whole polymers rather than fractions, leading to large uncertainties. Determinations such as these were rejected in favor of direct determinations of molecular weight by absolute methods such as light scattering or osmotic pressure.

The literature for atactic polystyrene has been critically reviewed and the K and a values for a variety of solvents often used for viscosity measurements have been recommended. The solvents are benzene, toluene, 1,2,4 trichlorobenzene, tetrahydrofuran (THF), o-dichlorobenzene, 2-butonone, and two theta solvents, cyclohexane and decalin. In addition, the Mark-Houwink parameters for several other solvents, not used as frequently, are provided. 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 poly(methyl methacrylate). The data for this polymer in 11 solvents are being reviewed. These are acetone, benzene, chloroform, butanone, THF, toluene, nitroethane, ethyl acetate, acetonitrile, dichloroethane, and methyl isobutyrate, as well as a number of theta solvents.

Self-Calibrating Gel Permeation Chromatography

Gel permeation chromatography (GPC) is a widely accepted technique for estimating the molecular-weight distribution (MWD) of high polymers. However, the usefulness of the conventional GPC apparatus is limited by the need to provide calibrants for each polymer measured of known molecular weight over the entire molecular weight range in which the MWD is significantly different from zero. The calibration depends, among other things, upon the chemical nature, degree of branching, etc., of the polymeric material so that each new material requires a fresh calibration. The so-called "universal calibration" hypothesis, while useful, is limited to comparisons of polymers of similar shape and, in any event, is inadequate for quantitative determinations. Some instruments, one of which is commercially available, are intended 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 builtat NBS 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.

A new sample injection system has been designed by us and installed which permits quantitative injection of samples into the GPC columns and injection of calibrants etc. directly into the light-scattering detector, bypassing the columns.

Diffusion of Linear and Cyclic Polymers in Semi-dilute Solutions by **Photobleaching Method**

Although the reptation model of de Gennes successfully accounts for the diffusion of linear polymers, there remains a controversy whether it adequately describes the diffusion of cyclic or star-shaped ones. Resolution of this controversy has been hampered by the lack of a rapid method for determining the diffusion coefficients of polymers and by the difficulty in preparing and purifying cyclic polymers. We have recently applied a novel method, called Fluorescence Recovery After Photobleaching (FRAP), to rapidly determine the diffusion coefficients of linear and cyclic polymers in semi-dilute solutions. The FRAP method can be used to measure diffusion coefficients in the range 10^{-11} to 10^{-6} cm^2/s.

Linear and cyclic polystyrene polymers of narrow molecular weight distribution have been labelled with nitrobenzoxadiazole (NBD). The diffusion of NBD-labelled cyclic polystyrene in dilute and semi-dilute linear polystyrene solutions has been measured by the FRAP method over a concentration range from 0.02 to 0.3 g/ml. No significant difference has been found between the diffusion of the cyclic polystyrene polymer and the diffusion of the linear polystyrene polymer when they have the same molecular weight.

Fluorescence Spectroscopy of Rod-like Polymers

Recently, heterocyclic rod-like polymers, exhibiting thermal and oxidative resistance as well as superior mechanical properties, have attracted considerable interest. The high strength of these polymers arises from their ability to achieve a high degree of molecular order during film or fiber processing. Such order arises from the high degree of rigidity that these polymers show as well as the degree of interaction they 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 solutions of the polymers, we hope to provide an estimate of the torsional rigidities of these polymers which we expect will relate directly to their performance properties. From studies of the fluorescence of the solutions of these polymers as a function of concentration, we hope to characterize the polymer-polymer interactions as well as the degree of order in the various phases.

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

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

We have also measured the lifetimes of electronically excited PBT and t-bisthiazole in methanesulfonic acid by nanosecond fluorescence spectroscopy. The lifetimes are estimated to be 0.2 to 0.3 ns for t-bisthiazole and 0.1 ns or less for PBT. We plan to get better estimates of the lifetimes by picosecond fluorescence spectroscopy.

Fluorescence Studies of Polymer Solutions

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

Translational Diffusion Constants of Linear and Branched Chains

With the advent of experimental equipment in which both static and quasi-elastic light scattering may be done on the same sample, the ability to obtain both a radius of gyration and a hydrodynamic radius on the same system is possible. For branched chains this 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 discrepancies. 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 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 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 coefficient are included in the modeling. Current work shows 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

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.

We have examined the concentration dependence of the translational diffusion constant of polymer chains in non-dilute solutions by direct computer simulation for simple lattice-model chains. In agreement with several recent experimental studies, the results show no sign of regions of constant power-law dependence of diffusion constant upon concentration predicted by some theoretical models. These results also appear to suggest that the major part of the concentration dependence may be accounted for by simple free-volume considerations.

Chemical Durability

Subtask 2 of Task 14332

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Work in this Subtask proceeds primarily along two lines: kinetics and mechanisms of polymer degradation and diffusion of additives in polymer matrices. The experimental study of the durability and legibility of polyester based recording media will lead to a lifetime prediction method that will help the National Archives determine when the archival microfilms and magnetic tapes should be copied. The experimental study of the degradation of poly(methyl methacrylate) will result in a predictive method for the lifetime of this material in outdoor applications. Since almost all polymers in use contain additives to maintain and enhance their useful properties, the experimental study of the diffusion-controlled formation of photodimers in polymer matrices will provide the data needed for predicting the lifetimes of polymers containing additives. Finally, the newly developed computer programs for gel permeation chromatography will facilitate the molecular weight determinations frequently needed for polymer-degradation studies.

Predicting the Lifetime of Polyester-Based Recording Media

Recording media have information-bearing coatings on a base of poly(ethylene terephthalate). Our earlier work has shown that the base polymer will last for 1000 to 2000 years at 20-25 °C and 50% relative humidity. The primarily polyester polyurethane tape binder which holds the oxide on the tape degrades severely under mild conditions by hydrolysis of the ester bond.

Magnetic tape binder is cross-linked, and is not completely soluble in any solvent. Other workers have reported that the soluble portion of binder increases at high relative humidities due to hydrolytic scission of the ester linkage, but decreases at low relative humidities due to the reverse of this reaction. They concluded that magnetic tape should be stable indefinitely at 20 °C and 40% relative humidity. We found at low relative humidity that magnetic tape binder cross-links further while polyester polyurethanes and undegraded model tape binder do not. Thus, the prediction of infinite stability, based on the concept of simple reversal of hydrolysis in model compounds, may not apply to magnetic tapes. We are currently aging tapes on which data have been written and are testing the readability of the tapes with a recently acquired commercial tape transport. The tapes soon became unreadable at 85 °C, the actual time depending on the level of relative humidity. None of the pre-written tapes has become unreadable when kept at 35 °C or lower temperatures, but tapes aged at 35 °C and 100% relative humidity for over 2 years and started before the tape transport became available can either not be written on successfully or require an abnormally large spacing between data.

The force required to peel the binder layer from the base and the elongation at which the binder layer breaks loose from the base when the tape is stretched decrease greatly with aging. The water uptake of the tape at different relative humidities increases somewhat with aging. These quantities can be measured on relatively small pieces of tape and will be used to predict the tape lifetime.

Degradation of Poly(methyl methacrylate)

The thermal degradation of commercial PMMA at temperatures up to 125 °C has been followed using gel permeation chromatographic determinations of molecular weight from which the number of chain scissions in the PMMA molecules is calculated. Gas chromatography has been used extensively to monitor the levels of small molecules in PMMA during degradation, and the results have been correlated with UV spectral measurements. Comparison of results from commercial and purified specimens showed that the degradation is initiated by some small molecular weight material which can be extracted from the PMMA using methanol. The low molecular weight material, which initiates degradation, is definitely not monomer nor methyl pyruvate. We have found no evidence for peroxide linkages in PMMA, which would decompose thermally to give chain scissions and methyl pyruvate. Our results suggest that the agent which initiates thermal degradation in PMMA at these temperatures is an oxidation product of molecular weight of 116 or 116x2, which is closely related to monomeric methyl methacrylate. We have shown that once scissions occur in PMMA, the monomer concentration approaches the level of 0.3% required by the equilibrium between propagation radicals and monomeric material. In the presence of oxygen and when the concentration of monomer is above 0.3%, the oxidation product is formed faster than it is destroyed, and the degradation rate of PMMA increases with time. As a steady state in the concentrations of monomer and oxidation product is approached, the degradation rate also becomes independent of time. In the absence of oxygen, additional amounts of oxidation product are not produced and the degradation rate falls with time. Publications dealing with the techniques of analysis, the combined effects of photo and thermal degradation, and lifetime prediction are planned.

Photodimers in Polymer Matrices

The photodimers formed by polycyclic aromatic hydrocarbons and their derivatives can be photodissociated to the original monomers. When the photodimer is held in a sufficiently 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 have measured the photophysical properties of the photodimers of anthracene and octadecyl anthroate. We have found that when a poly(methyl methacrylate) film containing dianthracene is exposed to UV light at 280nm, dianthracene dissociates to form anthracene. A readily measurable fraction of dianthracene is recovered when the film is subsequently irradiated with UV light at 365 nm.

Computer Programs for Gel Permeation Chromatography

Many special features have been incorporated into our GPC computer programs. We anticipate that these computer programs will be useful to the coatings industry, which routinely tries to compare chromatograms. Calibration of the GPC columns is a problematic step. The chromatograph can be calibrated from a single standard sample of wide molecular weight. The peak positions of narrow molecular weight standards can be picked out of their chromatograms automatically. A powerful least squares program allows easy and rapid comparison of observed and calculated quantities in the estimation of the 5-degree polynomial used to represent the calibration function of the columns. The user interacts with the calibration calculations to throw out bad points, examine the fit in detail, and quickly get a good calibration while having some feeling for what he is doing. The data collection program also invokes the data analysis program so that analyses can be made immediately after the data have been collected without operator intervention. To make this possible, the data analysis program contains a procedure which determines the limits of the peak in the chromatogram and estimates the best place at which the baseline may be determined.

Specimens may be characterized in terms of elution volume, which is dependent on the calibration of the columns, or log hydrodynamic volume, which is independent of the calibration of the columns. This latter method allows the meaningful comparison of chromatograms taken on different sets of columns, or at different times on columns, which are changing in calibration. Averages analogous to the various molecular weight averages are calculated from the distribution of hydrodynamic volumes. This allows quantitative comparisons to be made. Specimens for which Mark-Houwink parameters are available may also be characterized in terms of their molecular weight distributions and averages.

A program has been written to allow quantitative comparison and manipulation of chromatograms. This procedure was designed for specimens for which molecular weight distributions can not be calculated, either because the Mark-Houwink parameters relating hydrodynamic volume to molecular weight are not known, or, more often, because the chromatograms are from materials which are mixtures or branched or curing crosslinked polymers. A similar program has also been written to allow quantitative comparisons of molecular weight distributions, to produce compound molecular weight distributions from those of single components, and to decompose multicomponent molecular weight distributions into components. This program examines the shape of the molecular weight distribution and allows one to examine the calibration of the columns in this way.

BLENDS PROCESSING
Task 14333

Approximately 15 to 20% of the estimated 47 billion pounds of plastics to be produced in the United States during 1985 will be polymer blends. In the same way that stainless steels are alloys of iron, chromium, and nickel to make metal resistant to corrosion, polymer blends are a mixture of two or more polymers to create plastic alloys with new properties. Mechanical properties, flame retardance, processability, as well as many other polymer properties can be improved by blending.

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

To obtain basic information for predicting whether or not polymers are miscible and will mix together to form a homogeneous alloy and to control the rate of demixing and the size of phase separated microdomains if the polymers are immiscible, two research techniques are being used: small angle neutron scattering (SANS) and temperature-jump light scattering (TJLS). These methods allow the phase diagram to be determined and the phase separation kinetics to be studied. In addition to these two methods, Forced Rayleigh Scattering (FRS), small-angle X-ray scattering (SAXS), and electron microscopy are also used in polymer-blend studies.

FY 85 Significant Accomplishments

- Temperature, composition, and molecular weight dependences of the binary interaction parameter, χ, have been measured by small-angle neutron scattering for the first time for a binary polymer blend (polystyrene/poly(vinylmethylether) (PS/PVME). Using a new experimental technique developed at NBS, TJLS spinodal decomposition has been clearly observed in PS/PVME blends over a period of hours. At later stages, a hydrodynamic mechanism dominates the phase separation process. In this mechanism surface tension forces drive the phase separation and the domains grow linearly with time.

- The phase diagram, crystallization kinetics, and morphology of the polyvinylidene fluoride (PVDF) and polyethylacrylate (PEA) blend system have been determined. This system exhibits overlapping phase separation and crystallization behavior with the intersection of the cloud point and melting point curves occurring at about 180 °C and at a composition of 50/50 PVF_2/PEA (by weight). The binary interaction parameter, χ, measured from the PVF_2 melting point depression is −0.16 (at 170°C). The crystallization kinetics and morphology studies performed on blends

containing less than 50% PVF_2 yield information on the concentration dependence of the crystal growth rate, crystal habit, and lamellar structure in PVF_2.

- Scattering functions (monomer-monomer correlation functions), stability limits (spinodals), and the periodicity of mesophases have been calculated for block copolymer/homopolymer blends, graft copolymers, and n-armed diblock copolymers. A graft copolymer is more difficult to phase separate than a diblock copolymer of the same composition. A n-arm diblock copolymer (n = 1,2,..) with each arm having equal amounts of A and B monomers, phase separates at the same temperature for all n.

- A new facility for obtaining x-ray pole figures on specimens of semicrystalline polymers was implemented. This facility has been extensively used to characterize the orientation present in sheets of piezoelectric polymers and in thin films of polyethylene. Major components of the 10-meter small-angle x-ray scattering camera have arrived and are being installed. This camera is expected to be placed in service early in FY 1986.

Experimental
Subtask 1 of Task 14333

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Polystyrene/Poly(vinylmethylether) Blends

Twenty years ago, John Cahn of IMSE developed his now classic theory of spinodal decomposition (SD). In the intervening years experimentalists have searched for examples of this phase separation mechanism in both ceramic and metallic systems. Although the theory is widely accepted, experimental evidence to support it is sparse. Unequivocal experimental evidence of SD has now been found in PS/PVME blends.

PS/PVME blends exhibit lower critical solution temperatures at about 150°C. Small angle neutron scattering was used to determine for the first time the equilibrium phase diagram and the spinodal lines for this system. SANS was also used to determine the χ interaction parameter as a function of temperature and composition. The phase separation kinetics were measured using a temperature jump light scattering technique. Spinodal decomposition has been observed in the PS/PVME blend over a period of hours and the characteristic spacing of the SD network is of the order of 1 micrometer. Cahn's theory has been stringently tested and is able to describe the experimental observations in detail.

At a well-defined time, which is determined by the size of the temperature jump into the two-phase region, another mechanism of phase separation supercedes SD. This transition is marked by the feature that domain sizes now increase linearly with time. This is quite unlike the classical Lifshitz-Slyozov mechanism of phase ripening where domain size increases with the cube root of time. This new mechanism is dominated by hydrodynamics in which surface tension drives the phase separation. This hydrodynamic mechanism was first suggested by Eric Siggia at Cornell. Again the PS/PVME system appears to provide the best experimental evidence for the existence of this particular mechanism of phase separation.

Poly(vinylidene fluoride) and Poly(ethylacrylate) Blends

A partially miscible blend system consisting of a crystallizable component (PVF_2) and a noncrystallizable one (PEA) has been studied with the goal of determining the phase diagram. In order to establish the phase boundaries, the cloud point curve and the equilibrium melting point curve were determined. The melt exhibits phase separation upon heating (indicative of a lower critical solution temperature) to 10-50°C above the melting point of the PVF_2, depending on the composition. The cloud point and equilibrium melting point curve intersect at about 180°C and a composition of 50/50 (by weight) PVF_2/PEA.

The polymer-polymer interaction parameter, χ, was calculated from the equilibrium melting point data from samples containing 50% PVF_2 and less. The value obtained was -0.16 at (170°C), which is consistent with the miscibility of the blend in this composition range.

In addition to the phase diagram, the morphology of PVF_2 crystallized from the homogeneous melt (<50% PVF_2) has been studied. Spherulite growth rates for the alpha crystal form of PVF_2 have been measured as a function of composition and temperature. Analysis of the data yields a value of the product of the surface free energies $\sigma\sigma_e = 4 \times 10^{-4}\ J^2/m^4$ (assuming regime II kinetics) which appears to be independent of PEA content. While the spherulite growth rates depend only moderately on composition the spherulite morphology changes substantially with the texture becoming more open and the spherulite ring spacing becoming larger with increasing PEA content at a given crystallization temperature. At very low PVF_2 contents (0.5%) and relatively high crystallization temperatures (T_c = 150°C) single crystals of alpha-PVF_2 are formed. The basic crystal habit is diamond shaped bounded by four (110) faces and with the long axis of the crystal corresponding to the b axis of the unit cell. At lower crystallization temperatures enhanced dendritic growth occurs along the b axis, which also corresponds to the radial growth direction observed in alpha spherulites.

Future work will center around understanding the lamellar morphology of the spherulites grown in more concentrated blends (>15% PVF_2) and in following the evolution of the spherulites from simple lamellar crystals to more complex aggregates (and eventually spherulites) as the PVF_2 concentration is increased.

Theory

Subtask 2 of Task 14333

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Effect of Molecular Weight Distribution on Equilibrium Compositions of Polymer Blends

Flory-Huggins thermodynamics have been applied to the problem of equilibrium compositions of polymer blends with any molecular weight distribution. A numerical solution can be obtained giving the volumes, average compositions, and molecular weight distributions of the phases in equilibrium.

The calculations are greatly simplified by taking the limit of one of the phases going to zero volume. This corresponds to the experimentally accessible cloud point. The cloud point at the critical point is dependent on the weight average molecular weights. Away from the critical point, the cloud point diverges from the values calculated by assuming that the weight average acts as a monodisperse polymer of that weight. In the case where the amount of one of the polymers in the blend becomes small, the cloud point is affected greatly by the highest molecular weight portion of the distribution.

Effect of Sequence Distribution on the Miscibility of Polymer/Copolymer Blends

Previous theories describing the phase behavior of copolymer blends have ignored the sequence distribution of monomer units in the copolymer. We introduce a parameter, θ, which describes the binary sequence distribution of the monomers in a copolymer chain; $\theta=1$ for an alternating copolymer, $=0$ for a block copolymer, and $=1/2$ for a random copolymer. It is assumed that the interaction energy between a monomer of homopolymer C and the monomer A (or B) in the copolymer AB is mediated by the nearest neighbors chemically bonded to the A (or B) structural unit. It is found that the sequence distribution significantly affects the degree of compatibility between the polymers AB and C. For a fixed composition, there is an optimal range of θ values (or sequence distributions) for which the C/AB system is miscible.

Block Copolymer/Homopolymer Blends

The general phase diagram of a blend of a AB block copolymer and a homopolymer has been calculated. The mesophase transition temperature of the block copolymer may either increase or decrease when the copolymer is blended with a small amount of the homopolymer. When larger amounts of the homopolymer are added, a liquid-liquid phase transition may occur. All of the appropriate scattering functions (monomer-monomer correlation functions) and mesophase periodicities have also been calculated.

Phase Behavior of Graft and Star Diblock Copolymers

Scattering functions, mesophase periodicities, and limits of phase stability (spinodals) have been calculated for graft copolymers and n arm star diblock copolymers. The fraction of A monomers in the graft copolymer of the AB type is f and θ is the fraction along the A chain backbone at which the B chain is chemically linked (when $\theta = 0$ or 1 the graft copolymer becomes a diblock copolymer). Leibler has previously shown that when $f = 0.5$ that a diblock copolymer containing N monomer units undergoes a mesophase transition when $\chi N = 10.5$. According to the present theory, a graft copolymer with $f = 0.5$ and $\theta = 0.5$ is more difficult to phase separate and its critical χN value is 13.5. The critical χN values monotonically decrease to a value of 10.5 as θ approaches 0 or 1. In view of this result it is indeed surprising to find that for a star polymer in which each of the arms are block copolymers of composition $f = 0.5$, the critical χN value is always 10.5 independent of the number of arms, n.

Long Time Relaxation in Polymers Undergoing Phase Transitions

The kinetics of phase transitions is an important subject that is now just beginning to receive the attention that it deserves. Normally, the rate of forming new phase is faster the larger the supercooling (or more generally the thermodynamic force), however there are situations in which the phase may be locked in kinetically. As an example consider a chain that reptates in a potential field. The rate of reptation is less the larger the field gradient because the chain tends to get stuck in the deeper wells. Thus the rate of formation of the new phase will be inhibited. A good model is a periodic ramp potential. The slope of the ramp is proportional to the thermodynamic driving force and tends to empty out the wells. However, the depth of the wells can also increase with the thermodynamic driving force so that trapping results. This general idea has been used to explain very slow melting in DNA. It probably can explain slow relaxations in glasses and the formation of gels.

It is now widely recognized that relaxation in polymers rarely displays exponential decay, and that many times, the Kohlrausch-Williams-Watts (KWW) form $\exp(-t/\tau)^\beta$ is an accurate representation of the data where τ is the relaxation time and β a parameter between 0 and 1. Models of polymers that lead to the KWW form are being formulated. When the representative phase point must diffuse out of a deep well to effect a motion, and when there is a distribution in well depths, then we obtain KWW behavior.

Random Walk in a Random Array of Traps

We have obtained a generating function solution for a random walk on a one-dimensional lattice where the probability of stepping from lattice site i to site j is proportional to $\exp\{-a/(i-j)\}$ and where M lattice sites, $R_1 < R_2 < \ldots < R_M$, are designated as trapping sites. Among the many quantities of interest which we have evaluated are: (1) the probability of starting at an arbitrary point r_o in the presence of two traps and ultimately being trapped at R_1; and (2) the probability of starting to the right of M traps and ultimately ending up at a site to the left of the traps.

SAXS and Pole Figure Facilities

Subtask 3 of Task 14333

J. D. Barnes and D. F. Krintz

Digital Camera for Small-Angle X-ray Scattering

The small angle X-ray scattering laboratory is essentially ready to receive the 10-meter, small angle X-ray camera. The X-ray generator is in place on its rotatable mount, and the masonry piers for supporting the beam path have been installed. Most of the major components of the beam path have been built, and the entire camera will be installed as soon as the support for the entrance window and the specimen chamber come out of the shops. Electronic alignment of the detector system is underway. Further work on computer interfacing is required.

The software for the color graphics display system is essentially complete and supporting tools for statistical analysis and modelling have been installed on the VAX computer. Prototype versions of the software for the dedicated data-acquisition computer have been written. We will be writing software for integrated data collection, experiment control, and on-line data display shortly. The techniques used in our previous laboratory automation efforts will be used to provide simple operation of the system.

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

X-ray Pole Figure

The NBS Polymers Division has installed a new facility for obtaining X-ray pole figures on polymer specimens. Dr. Edward Clark, a consultant to the Division, provided material assistance in designing software to control data acquisition on this machine. Additional software for plotting the data has been implemented on the small angle x-ray data analysis facility. Users of the facility have collected more than 300 data sets since September of 1984.

The quality and quantity of the numerical data obtained with this facility have created a need for improved tools for describing the results. Dr. Clark has prepared a report on the use of orientation functions of various kinds to characterize the materials being studied. Dr. Clifford Speigelmann of the NBS Statistical Engineering Laboratory has been working closely with Polymers Division staff to develop suitable descriptive measures based on probability density functions defined on a spherical domain.

The NBS work in developing data descriptions based on explicit probability density functions is pioneering work that should provide data that can characterize the products of materials forming processes in a more morphologically descriptive way. This approach contrasts with the standard technique of calculating orientation functions from data with lots of noise. The new approach produces functions that have all of the correct characteristics of pole figure data in that they are smooth non-negative functions whose integral over the surface of the sphere is finite. Because these probability density functions are defined on a spherical domain, they also possess all of the correct periodicities. Suitable statistical estimation techniques can be used to determine the values of width parameters, location parameters, and other characteristics of the distributions.

Initial applications of these modelling techniques to the study of piezoelectric activity in polymers and to the study of orientation in blow-molded films are encouraging. Future efforts will be devoted to finding functions that fit the data better and to applying these techniques to inverse pole figures.

The pole figure facility has created a need for software to calculate structure factors, absorption corrections, and plots of molecular structures. We are implementing these tools on the VAX as they are needed. In some instances we must adapt software used for work with single crystals to deal with the kinds of specimens that we use in our work. Absorption corrections are a good example because the usual software does not deal with the finite size of the incident beam.

Before the data from the new pole figure system can be regarded as truly quantitative, we must develop procedures to correct for background and absorption. Techniques for resolving contributions from overlapping diffraction maxima are also needed. We expect to pursue design studies aimed at adapting a one-dimensional position-sensitive detector to the apparatus. We expect to improve our background estimates by collecting data over a range of angles around the diffration maxima of interest. We should also be able to resolve overlapping peaks and to simultaneously collect data from multiple reflections. The diffraction geometry for such a system is complex because the data from different parts of the detector arises from different chi and phi values.

BIOMATERIALS SCIENCE, METROLOGY AND STANDARDS FOR IMPROVED DURABILITY, APPLICATIONS AND MANUFACTURING OF DENTAL AND MEDICAL MATERIALS

Task 14335

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, there are plans to include these activities in the future.

Materials-research efforts are aimed at development of materials and techniques for promoting adhesion of restorative materials to tooth dentin and enamel. Novel approaches are pursued for reducing marginal leakage of restorations via utilization of adhesives and durable space occupying materials for use in cavity preparations. These include new composite resin formulations with reduced polymerization shrinkage and more resistance to attack by oral fluids as well as macroscopic bulky space fillers bonded to cavity walls. Strong, more durable, versatile dental cements are also explored as are methods for improving properties of surgical bone cement such as durability, radiopacity, and coupling between the bone-metallic implant system. Studies of calcium phosphate compounds for endodontic sealants, bone augmentation, or caries-reducing agents are being investigated. The basic chemistry of precipitation of calcium phosphates is explored as it relates to formation of mineral deposits such as bone, teeth, and atherosclerotic plaque is under investigation.

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

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

FY 85 Significant Accomplishments

- Cooperative work with an American company lead to the development of a new casting investment suitable for titanium metals and the clinical placement of the first-known dental titanium casting in the United States. General effects of variables such as casting investment on precision casting of dental alloys were also identfied.

- Tough, deformable dental-cement formulations which expand slightly on setting have been developed. Prepolymer resins for dental composites which reduce polymerization shrinkage and show promise for higher in vivo durability were also developed. These include monomers which expand during free-radical polymerization. A dental composite using a glass filler developed at NBS was made commercially available by American Industury.

- A hardening calcium phosphate cement (using only calcium phosphate compounds) suitable as an endodontic sealant and with other potential biomaterial applications have been developed. Monomers which yield surgical bone-cement radiopaque were also synthesized. A new dental cement with improved adhesion and durability was developed. The iron cation species responsible for bonding between dentin, a surface active compound and a coupling agent of a dentin bonding system was also identified. This coupling agent was developed at the American Dental Association Health Foundation, Paffenbarger Research Center (ADAHF/PRC) at NBS.

- Some service conditions under which dental glass-ionomer cements are prone to catastrophic failure have been identified. Along similiar lines it was demonstrated that dental composites evaluated by diametral tensile testing undergo surface induced failure rather than internal-flaw induced fracture.

Dental Composite and Cement Sealant and Adhesion Chemistry

Subtask 1 of Task 14335

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Vinyl-based thermosetting composites, the primary esthetic anterior dental restorative material, also are increasingly being used in stress-bearing applications traditionally reserved for amalgam fillings. However, despite recent improvements in many properties of dental composites, they still are deficient in wear resistance and margin adaptability. Recent research at NBS has indicated that the oral environmental resistance (OER) of polymer-based dental materials is a significant factor in determining their *in vivo* performance and ultimate service life both in relatively stress-free as well as stress-bearing situations. To enhance the OER of these materials two complementary approaches are being pursued in our laboratories. One approach is designed to increase the degree of polymerization and crosslink density of dental vinyl-resin systems by the synthesis and formulation of flexible, multifunctional methacrylates and chain transfer agents (e.g. polythiols). The other approach involves designing resin systems that have solubility parameters significantly lower than that found in the oral environment. To this end we have synthesized and formulated resin systems that yield composites containing significant amounts of fluorocarbon or siloxane segments in the matrix phase and still have acceptable mechanical properties. Composites prepared using a siloxane-containing resin showed improved OER and acceptable strength. Emphasis also is directed to monomer systems that have minimal (preferably zero or slightly positive) changes in volume on polymerization. The difficulty of increasing the degree of polymerization while simultaneously minimizing polymerization shrinkage is recognized. Two methods are being pursued, (1) the synthesis of prepolymer monomers and (2) monomers that expand on polymerization. A polyfluorinated oligoether with pendant urethane ethyl methacrylate groups (PFUMA) was synthesized which on formulation yield composites with excellent esthetics and mechanical strength comparable to commercial composites. These low surface-energy resin-based composites also exhibit low water sorption, residual unsaturation, and polymerization shrinkage. A new synthetic procedure has been developed which permits the formation of free-radical polymerizable, asymmetric spiro orthocarbonate monomers which expand upon polymerization. A series of these monomers containing various substituent groups has been prepared. Formulations comprised of these spiro monomers in conjunction with commercial monomers common to dental composites and adhesives are under evaluation.

In another study the chemical stability of dental resin is being investigated regarding (1) the color changes of a wide variety of dental resins resulting from the exposure to different radiation sources or to thermal exposure, under diverse environmental conditions for various periods of time, (2) correlation of the experimental aging test results with the composition of the materials as well as with its clinical performance. It was found that dental compositieswith are more susceptable to undergo color changes on aging than denture-base resins or plastic teeth. Therefore, a series of composites were exposed to the Xenon or RS lamp for time periods ranging from six hours to seven days. Composites were also aged at 60 °C in the absence of light. The ingredients of the materials studied are currently being analyzed by liquid chromatography and infra-red analysis. The results of this investigation should establish which constituents cause the color instability of dental composites.

A main disadvantage of most dental restorative materials is the lack of adhesive bonding to tooth structures in the oral environment. Investigation continues on the materials and methods of the ADAHF bonding system which has been shown to chemically unite composite resins to dentin as well as to enamel. The bonding system consists of treating the tooth surface with an aqueous solution of ferric oxalate, rinsing with water, and then applying solvent solutions of a surface-active compound and a coupling agent, one after the other. This treatment prepares the surface for very strong adhesive bonding with composites. Recent studies have centered on determining the best level of acidity of the ferric oxalate solution. The same degree of acidity gave maximum bond strengths to both enamel and dentin, a fortunate coincidence. Mossbauer spectroscopy has been used to study the role of the iron (ferric ion) component in this new adhesion technology. This spectroscopy has given information regarding the nature of the immediate chemical environment of the iron cation as it reacts with the tooth surfaces and the other components. Also, other methods have been used to determine the nature of complexes which form between the iron, the surface-active compound and the coupling agent. For the ultimate clinical success of this new capability, it is essential to clearly characterize the structural modifications of the tooth surfaces and the chemical reactions which the compounds undergo to bring about the initiation of polymerization of the active molecular species bound to the surfaces. Gratifying progress has been made during this year toward these important ends.

Experimental work on improving posterior-composite durability is exploring a glass reinforcing filler with a refractive index which renders composite restorations esthetically translucent, X-ray opacity, which improves diagnostic properties of the restorations, and phase separability, which makes it possible to acid etch the filler particles for improved bonding between glass filler and resin binder. The first commercial product based on this glass composition was introduced to the dental profession this year. The ADAHF/PRC at NBS obtained a patent on this product.

Another objective of this subtask has been to synthesize specific monomers or oligomers such as allyl 2-cyanoacrylate or oligomers of 2-isocyanatoethyl methacrylate and to prepare suitable formulations using these ingredients which may bond to dentin in an aqueous environment. A neat monomer of allyl cyanoacrylate adhered to biosurfaces. However, the storage stability of the inhibited monomer even when refrigerated was only a few months. A copolymer of n-butyl methacrylate (35 wt %) ethyl acrylate (35 wt %) and 2-isocyanatoethyl methacrylate (30 wt %) was also synthesized. The vitreous colorless solid containing pendant isocyanate groups as established from infra-red spectra will be reacted with mineralized tissue such as bone or dentin to determine if grafting of this polymer and collagen-containing surfaces takes place.

Non-eugenol containing dental cements based on vanillate esters, o-ethoxybenzoic acid (EBA) and zinc oxide, have also been developed in this laboratory. These cements have many advantages compared to the presently used zinc oxide-eugenol (ZOE) or EBA cements: (1) excellent strength, (2) lower solubility, (3) cure in conjunction with composite filling materials to which they adhere, (4) are compatible with acrylic monomers, (5) adhere strongly, in water, to non-precious metals, procelain and composites. The present objectives of this study are to modify these cements by additions of small concentrations of additives such as acids, metals, or fluorides to improve their properties. Hexyl vanillate or ethylhexyl syringate cements that are prepared with fluoride salts could possess caries reducing properties. The biological safety evalution of the hexyl vanillate (HV)-EBA-ZnO cements have been completed and the cements are now considered safe for clinical studies.

The feasibility of utilizing halatopolymers derived from dimer acid (DA) and trimer acid (TA) as the organic phases of dental cements is also being explored. A translucent cement which matches tooth color and resists brittle fracture under compression was made from DA and calcium hydroxide. This cement is hydrophobic, compatible with resin-based dental materials and, because of the alkaline constituents, it may promote secondary dentin formation. Reinforced DA/$Ca(OH)_2$ exhibited improved dimensional stability, and strength, low solubility and, in some cases, adequate radiopacity. Remarkably, some of these DA cement formulations expand slightly on setting.

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

Subtask 2 of Task 14335

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In our laboratories wear measurements have been extended to include ionomer cements. Prior to wear measurements the specimens were preconditioned in air, water, and 0.02 N lactic acid for one week. With the air-preconditioned specimens, wear studies were essentially impossible due to catastrophic failure resulting from brittle fracture of the dehydrated specimens. With the lactic acid preconditioning, the hardness fell markedly with a corresponding decrease in wear resistance. Since lactic acid is generated during plaque formation, it is intraorally omnipresent in many people. This kind of chemical instability is a serious limitation to the in vivo application of ionomer cements as presently formulated.

Experimental composites with flexible-chain polymers were evaluated. Specimens were preconditioned in organic solvents with solubility parameters encompassing those applicable to the intraoral environment. The results indicated that these composites softened by amounts similar to those observed on present commercial composite restorative materials; however, the maximum swelling corresponded to lower values of solubility parameters as intended.

Wear measurements were initiated on an experimental composite containing a 70/30 PFUMA/bis(methacryl oxypropyl) tetramethyl-disiloxane (BIS-MPTMS) matrix polymer. The specimens were preconditioned in 100% ethanol and in pure water for which the former produced a large amount of swelling and the latter, none. Although the wear rate for this material was larger than that usually observed for the commercial materials, it was essentially unaffected by preconditioning. This distinction between hardness and wear behavior may result from the high degree of crosslinking in this polymer and its more rubberlike character which allow softening, but limit decomposition or breakdown during wear. Studies of glass transition temperatures (T_g) are also considered important for characterization of wear test materials. T_g measurements are carried out using differential scanning calorimetric (DSC) and torsional rheometric (TR) methods. Specimens of 70% 2,2-bis[p-(2'-hydroxyl-3'-methacryl oxypropoxy)-phenyl]propane (BIS-GMA) - 30% triethylene glycol dimethacrylate (TEGDMA) were cured with benzoyl peroxide, over a temperature range of 37 °C to 183 °C. The TR results of the specimens cured below 100 °C indicated the existence of two glass transition peaks; the position of both peaks are somewhat sensitive to the curing temperature, T_c. Only one prominent glass transition peak could be observed for specimens cured above 100 °C. The value of the lower glass transition temperature for specimens cured at 37 °C is 55 °C, which is dangerously close to the service temperature.

With respect to recent public concern over potential health hazards caused by dental amalgams, considerable time and effort has been devoted during the past year to reviewing the literature and preparing lectures and papers related to the potential hazards of mercury or glavanism from these restorations. To date no evidence has been discovered that indicates hazard to the vast majority of patients.

On April 11, 1985, the first clinical cementation of a dental titanium casting in the United States was performed. This was the result of American Dental Association supported research. The casting has excellent margin adaptation and retention. The titanium is in approximal contact with a gold crown, and the occluding bicuspid has an amalgam restoration; yet, there is no galvanic response, unusual taste, or other problem related to the restoration. Additional castings are being made for other patients. A new investment material and casting technique unique to titanium that made this casting possible. (See Subtask 3)

Dental Alloys, Ceramics, Metrology, and Analysis

Subtask 3 of Task 14335

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The ability to cast new dental alloys into precise prosthetic forms is an important consideration. Using a technique developed here, a castability value C_v is defined as the number (or fraction) of completely cast segments from a polyester grid pattern. Recent work has focussed on determining the temperature dependent effects of various elements on C_{vt}, (a previously defined, statistically relevant transform of C_v). Boron was found to greatly improve C_{vt}, but as the alloy temperature was raised, its effect became less important. Silicon was also found to have a positive effect on C_{vt}, but its effect became more pronounced as the alloy temperature was raised. The effects of other elements as function of alloy and mold temperatures are being assessed. Preliminary studies also indicate that various batches of investment produce the same temperature dependent effects, but that there are shifts in the magnitude of C_{vt} with each batch for a given set of temperature conditions. To ensure control of the variable of casting force, the automatic centrifugal casting machine was instrumented to measure that force during the casting process.

Work continues to progress on development of technique and materials for making titanium dental castings. A new zirconium oxide investment material has been developed containing a proprietary additive for producing a predetermined expansion of the mold at its firing temperature. This permits casting of any metal or alloy into room-temperature molds without loss of dimensional accuracy. A dental crown of pure titanium has already been cast using this mold material and is presently undergoing a clinical study. This is the first clinical titanium casting ever used in the U.S. and it marks the beginning of more extensive studies in our ongoing research program on titanium dental castings.

Efforts on characterizing the strength of porcelain-metal system continues. Weibull statistical analysis shows three dental systems are not normally distributed. Progress is being made on implementing maximum likelihood algorithm for defining characteristic strength parameters. Porcelain-metal thermomechanical-stress compatibility also is being investigated. Finite-element programs are underdeveloped to account for thermal gradients and viscous stress relaxation during cooling from porcelain fixing temperature. This effort is in cooperation with the University of Illinois, Chicago.

The application of Weibull statistics for evaluation of the strength of dental composites is being explored. The high strength of an experimenal industrial composite material was shown by Weibull Statistics analyis to be the result of the non-standard (small) specimen size used by the manufacturer. The analysis suggests that the fracture initiating flaws are distributed on the surface of the specimen rather than through its bulk.

In a cooperative program with the University of Michigan the Diametral Tensile Test (DTT) was evaluated for applicability to the newer dental composite restoratives (DCR). Samples from four DCR's were tested at crosshead speeds from0.5 to 0.005 cm/min. All of the DCR's were more brittle than the brittle cement. It was concluded that the DTT remains a viable method for determining the tensile strength of the more recent DCRs.

Finally, a mercury dilatometer was constructed for measuring the polymerization shrinkage of commercial dental composites and newly formulated NBS dental resins, cements, and composites. This instrument will be a key measurement device for the program tasks aimed at improving such materials.

Calcium Phosphate Chemistry, Biochemistry, Structure and Clinical Implications

Subtask 4 of Task 14335

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An improved topical dental fluoridation procedure is being studied. In recent studies a treatment which forms dicalcium phosphate dihydrate in enamel was found to greatly increase enamel reactivity towards low levels (0.2 to 2 parts per million) of fluoride. Repeated treatment induces additional fluoride uptake. This treatment regimen would significantly enrich the tooth enamel with permanently bound fluoride and should enhance the tooth resistance to decay. This would constitute a fluoride-enhancing regimen without the use of additional fluoride applications.

Remineralization of white spot lesions also is being investigated. Slurries containing tetracalcium phosphate and dicalcium phosphate in a carboxymethyl cellulose gel were found to effectively remineralize artificial caries-like lesions in enamel. Because of the ease of handling, these slurries have good potential for remineralizing incipient lesions *in vivo*.

A hardening calcium phosphate cement consisting of only calcium phosphate compounds was developed during the previous report period. This cement has now been tested as an endodontic root-canal filling material in a pilot animal study. The results were often superior to those obtained with gutta-percha. Since the cement is highly biocompatible, it may prove to be permissible for the cement to protrude beyond the apical foramen without deleterious effects.

Ultramicro-analytical techniques previously developed for studies of caries mechanisms were applied to the analysis of plaque samples collected from individual sites in the human mouth. These analytical procedures permit determinations of the variation in parameters between adjacent sites in a single individual and facilitates studies of the mechanisms of caries and other plaque-induced oral diseases.

Investigation of octacalcium phosphate (OCP), a precursor in the formation of tooth mineral, and its role in biomineralization has continued. OCP forms crystalline adducts with a number of aliphatic saturated dicarboxylates. Based on the structures of OCP and calcium succinate a structural model for an OCP-succinate complex was proposed. Attempts are being made to prepare large crystals suitable for single-crystal studies of this complex as well as complex crystals containing other dicarboxylic acids. The unravelling of the mode of incorporation of these dicarboxylate ions into OCP could have a significant impact in the understanding of the chemistry of biomineralization and may have implications of value in adhesive-bonding technology.

Pathological calcification in the cardiovascular system is being studied. Extensive characterization of the mineral phase in cardiovascular plaque and solubility measurements of a number of calcium phosphates in blood and serum were made. During the present reporting period, we contributed substantially to the physical and structural information on plaque mineral. This information has major implications regarding pathological calcium phosphate deposits: (1) These deposits should not form unless the serum becomes supersaturated with respect to octacalcium phosphate. (2) According to our findings, serum is approximately saturated with respect to octacalcium phosphate and slightly supersaturated with respect to plaque mineral. Because of the close proximity of these values, it should be possible to manipulate the calcium and phosphate levels in blood relatively slightly so as to make it either undersaturated or supersaturated with respect to octacalcium phosphate and/or plaque mineral, as might be required by the disease conditions; with this knowledge, it may be possible to induce dissolution of mineral deposits or prevent their formation without the use of invasive techniques. (3) The roles of surface-active agents that block crystal growth of octacalcium phosphate or its conversion can be understood with greater precision. And (4) the chemical properties of these materials (e.g., reactions with F^-) and their manipulation in treatment regimens can be anticipated.

One principal objective of the research done under this subtask is to better understand biomineralization mechanisms. Current areas of interest include the nucleation/growth processes which occur during the initial stages of mineral deposition in vertebrate hard tissue, the physiochemical and structural properties of biological mineral and related synthetic salts, and the interaction of these salts with compounds of biological interest. There is growing evidence that the first mineral to form in cartilage, dentin, and some bone tissues occurs in association with submicron size, membrane-bound, extracellular structures known as matrix vesicles. A method developed by NIDR members of this group uses synthetic lipid vesicles (liposomes) to artifically duplicate many of the precipitation steps observed in matrix vesicle calcification. In previous studies using this method, it was shown that precipitation inside the liposomes involved the sequential appearance of three distinct calcium phosphate salts: amorphous calcium phosphate, octacalcium phosphate, and hydroxyapatite. Electron microscopic techniques showed precipitation of calcium phosphate salts was also found to disrupt the normally stable membrane envelope. This disruption enables the internal precipitate to induce additional precipitation outside the liposome as well. Since these events parallel in many ways those which occur in and around matrix vesicles, the liposome system provides a useful vehicle for investigating the role membrane constituents native to matrix vesicles may have in regulating these events. Results of studies involving phospholipids and liposomes may prove useful in assessing the role lipids have in coronary and vascular calcification.

A new study has been initiated on factors controlling apatite crystal growth. X-ray diffraction line broadening analysis is being employed to determine the size apatite crystals can attain under a variety of physiologically-relevant solution conditions. Particular effort is being directed toward elucidating the effect of fluoride ions in delimiting crystal growth. Results from this study should also provide new insight into the physiochemical processes controlling apatite crystal growth in biological tissues.

Hydroxyapatite is considered the prototype structure for the apatitic phases investing hard tissues. An important, ongoing area of research under this subtask is the preparation and detailed characterization of pure and compositionally modified (e.g. F, CO_3 substituted) hydroxyapatites suitable for use as standards and controls in studies on the structure and chemistry of tooth enamel apatite. In a recently completed study, data from synthetic hydroxyapatites were utilized to elucidate factors contributing to the reduced solubility of laser-irradiated enamel mineral. The understanding of such reductions in solubility is an important consideration in developing rational, effective clinical laser treatments for preventing tooth decay.

Improved Surgical Bone Cement
Subtask 5 of Task 14335

G. M. Brauer, J. W. Stansbury, and J. A. Tesk

The ever increasing use of plastics for medical and dental applications makes it desirable (often mandatory) that such materials have adequate radiopacity to detect their presence in various environments. Some commercial materials (e.g. bone cements) incorporate fillers of heavy metal salts such as barium sulfate or bismuth subnitrate which weakens the material. More compatible monomers with a high percentage of atoms of high moleular weight such as triodophenyl or pentabromophenyl methacrylate have been synthesized. These monomers are compatible with monomers used in bone cements and denture-base resins. The rate and kinetics of polymerization of monomer-polymer doughs is not altered appreciably. Addition of 10 to 15 percent of the brominated or iodinated monomer to methyl methacrylate results in radiopaque polymers. Such compositions are more homogeneous than filler-containing compositions and have higher strength than commercial bone cements with barium sulfate fillers. Other properties of these copolymeric compositions are being investigated.

MECHANICAL PERFORMANCE OF POLYMERS

Task 14336

The approximate 8% annual growth of polymeric materials results from substitution for other materials owing to enhanced properties at reduced costs, the expanded need for all materials due to growth in population and economic activity, as well as new products that rely on unique properties of polymers. Important to wider use and acceptance of plastics is a firmer understanding of performance limitations and processes that affect durability. Full exploitation of plastics has not been realized due to the lack of adequate data and models upon which to design for long-term use. 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 theories of bond rupture as models for degradation of mechanical properties and for extrapolating short-time measurements to predict long-term performance; (3) model mechanical properties behavior and failure using time dependent constitutive equations; and (4) expand fracture mechanics approach to viscoelastic materials to model craze and crack-growth phenomena.

Joint programs on performance of plastics have been established with other government agencies which are fostering the use of plastics in areas of national concern. 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 microstructural 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. Test methods for evaluating the performance of elastomers used in tank track pads are under development in a joint project with the U.S. Army tank & Automotive Command.

FY 85 Significant Accomplishments

- Solid state nuclear magnetic resonance measurements have been used to elucidate the dispersion of the rigid-rod molecule, poly(p-phenylbisbenzthiazole), in the molecular composite using polyamides as matrix materials. The degree of dispersion affects the mechanical properties of molecular composites.

- The creep and recovery behavior of polyethylenes under small uniaxialy deformations has been successfully described with a one-dimensional equation consisting of a single integral hereditary term and a plasticity term.

- The molecular structure and fine texture of polyethylene film used in heavy lift balloons has been identified. The uniaxial and biaxial behaviors of the same films have been determined to correlate structure with mechanical performance.

Characterization of Polymer Structure and Deformation Processes

Subtask 1 of Task 14336

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The identification of molecular mechanisms and changes in physical structure associated with deformation during and subsequent to processing not only provides the basis for development of test methods for prediction of long-term performance and for quality control, but also provides insights into the selection, processing, and design of materials with improved mechanical properties and performance. A key aspect is the development of advanced techniques to elucidate the molecular structure and fine texture of polymers. The nature of the organization of individual polymer molecules in the semicrystalline, lamellar textured morphology of the solid state is being addressed by model calculations of crystal growth and small angle neutron scattering profiles, as well as morphological studies of the crystal habits of polymer crystals.

Vibrational spectroscopy and solid state nuclear magnetic resonance are used to elucidate the physical structures of semicrystalline and amorphous polymers, as well as molecular composites. Calculational approaches are used to predict the spectral signatures of those crystal defects having the lowest conformational energies. Defects of this sort are thought to be involved in mechanisms associated with mechanical deformation, as well as other physical processes.

Techniques are under development to produce single extended polymer molecules on conducting substrates which are suitable for investigation by tunneling electron microscopy. By such investigations details of the type and distribution of branching in polymers as well as the architecture of copolymers may be elucidated. Better methods are needed to measure branching in polymers, as this aspect of molecular structure, such as in linear low density polyethylenes, can lead to enhanced mechanical properties.

Recently, large-scale polymer motion, as in self-diffusion, has been treated using reptation models which although successful at describing some aspects have failed to adequately predict others. Work is directed towards testing recent reptation models of polymer diffusion in the solid state and melt, as well as the discrepancy between the observed dependence of the melt viscosity on molecular weight and that predicted from reptation theories. The linear viscoelastic behavior of cyclic polymer molecules and their linear analogues has been determined as a test of reptation models since cyclic polymer molecules should exhibit quite different behavior than the linear analogues.

Chain Scission and Mechanical Performance of Polyethylene

The underlying chemical processes associated with mechanical degradation of polymers involve scission or rupture of valence bonds and/or van der Waals type bonds. The valence bonds comprise the skeletal backbone of the polymer while the latter type involve interactions between different polymer segments either on the same polymer or belonging to different polymer chains. The initial rupture of valence carbon bonds produces highly reactive primary free radicals which quickly undergo reactions to yield secondary free radicals. The nature of the free radical reactions is such that for most polymeric materials only the secondary radicals are observable by electron spin resonance (ESR). The secondary radicals undergo propagation and termination reactions to produce stable chemical species whose concentrations can be measured with infrared spectroscopy.

Infrared spectroscopy and ESR have been used to measure the levels of chain scission associated with mechanical stress and degradation. Studies have been conducted on polyethylene (PE) and polystyrene degraded by grinding under liquid nitrogen, as well as on PE ruptured under sinusoidal and constant loadings. Chain scission concentrations have been measured as functions of the number of cycles in fatigue experiments and of strain carried out using a stretching frame.

In the present work, we investigated the dependence of chain scission on strain produced under sinusoidal loadings (fatigue). This work was motivated by the following observation. Whereas the buildup in chain concentration increased with the number of stress cycles in a fatigue experiment, no detectible chain scissions were observed in specimens deformed in a stretching frame up to the point of macroscopic rupture. After macroscopic rupture the chain scission concentrations were similar to those observed after rupture in fatigue experiments.

The fatigue experiments were carried out at constant peak stress and the specimens underwent plastic deformation during the experiment. The specimen elongation and chain scission concentration were measured as a function of the number of fatigue cycles in separate experiments. In this manner, the chain rupture concentrations could be plotted as a function of the elongation in a fatigue experiment and the results compared to those obtained by deforming the polymer in a stretching frame. Data were obtained at both 0.01 and 0.002 Hz.

Somewhat different results were observed at the two frequencies. At 0.002 Hz no increase in chain scission concentration was observed up to a strain of 2.5, followed by an abrupt rise, and a plateau region until the strain reached a value of 4. The chain rupture concentration then increased linearly up to the rupture strain. At the higher frequency, 0.01 Hz, the chain scission concentration increased linearly with strain up to a strain of 2.5, followed by a steep rise, and another region of linear behavior up to the strain at rupture. The steep rise is a common feature of both sinusoidal loading frequencies. Current work is directed towards developing a model of polymer deformation that adequately describes these observations, as well as those obtained under quasi-static conditions.

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

This project is a joint effort with the Air Force Materials Laboratory to facilitate development of high strength polymeric materials for use in structural elements of airplanes as well as other military goods. The Air Force is 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 moieties are exceedingly stiff and tend to form rod-like macromolecules. These polymers are difficult to process and generally must be solution cast from strong acids. In order to increase the ease of fabrication of these materials while taking advantage of the inherent reinforcing capabilities of stiff, rod-like molecules, there has been considerable effort to develop high strength composites by blending these rod-like molecules with more flexible macromolecules. The reinforcing efficiency of the rod-like component depends rather crucially on whether the rods aggregate (low strength) or are well dispersed (high strength). We are using advanced proton and C-13 solid-state NMR techniques to measure the intimacy of mixing of the two components in molecular composites.

While problems relating to the variable levels of proton-containing impurities render certain NMR approaches to this question impossible, a significant measure of success was realized in the characterization of a composite of nylon 6,6 and poly(p-phenylbenzbisthiazole) (PBT). In a 40% nylon/60% PBT sample coagulated out of methane sulfonic acid, washed in water, and compression molded at 255°C, mixing was shown not to occur at the molecular scale. Minimum domain dimensions were determined to be in the 4-5nm range for both components with some possibly larger nylon crystalline regions. Rates of proton spin diffusion between the nylon and PBT domains are the NMR observables which yield minimum domain dimensions.

The observation of significant concentrations of mobile-proton containing impurities in the coagulated and washed samples of both rigid-rod homopolymers and molecular composites requires further investigation. The entrapment of impurities prior to heat treatment may lead to unwanted chemical reactions during heat treatment. Also, impurities could aggregate during heat treatment and prevent longer-range structural ordering, thereby limiting the attainable mechanical properties.

Partitioning of Chain Ends and Side Groups Between the Crystalline and Non-Crystalline Regions of Melt-Crystallized polyethylenes

The concept of proton spin diffusion in solid polymers may be used to argue for the nearly uniform spin temperature of adjacent chains. This assumption, along with the ability to distinguish vinyl and methyl end-group resonances and ethyl and methyl branch resonances from backbone resonances in magic-angle sample spinning (MAS) C-13 spectra enable the spectroscopist to locate chain ends or side branches with respect to the crystalline or non-crystalline regions.

By suitably changing the preparation of proton magnetization prior to cross-polarization (by which C-13 signals are generated), different mixtures of crystalline and non-crystalline signals may be obtained and through appropriate linear combinations of these spectra, "pure crystalline" and "pure non-crystalline" signals may be determined. With an independent knowledge of end group and side-group concentrations, the partitioning of end groups and sidegroups between the crystalline and non-crystalline regions is obtained.

In a linear polymer, more than half of the methyl ends reside in the crystal. For terminal vinyl groups on the order of 40% are to be found in the crystal. This is a substantially higher fraction than is found by other workers in solution-grown crystals. In those studies only 2-15% of vinyl ends appear to be unavailable for chemical reaction with bromine or ozone.

With respect to side branch incorporation in the crystal, preliminary results indicate that methyl side branches are incorporated to a much greater degree than ethyl side branches. The ethyl branches seem to be rejected by the crystal rather completely, i.e. 90-95% of the ethyl branches are in the non-crystalline region.

We have also examined some radiation effects using these techniques since sol and gel fractions can be simultaneously examined. Aside from the rather quick disappearance of terminal vinyls upon gamma irradiation and the buildup of non-terminal vinyl groups and methyl end groups, little can be observed. The radiation-induced interior vinyls seem to be evenly partitioned between the crystalline and non-crystalline phases.

Second-Order Dipolar Shifts for C-13 Nuclei in Solids

A small, but real, contribution to the chemical shift for protonated carbons has been shown to be attributable to a second-order perturbation contribution from a non-secular term of the carbon-proton dipolar interaction. The importance of this contribution diminishes as one moves to higher static magnetic fields. The recognition of the shift provides the basis for a more accurate comparison of shift data obtained at different magnetic fields. It also enables one to separate those influences on chemical shifts due to structure and conformation (effects considered interesting) from those which depend merely on the operating magnetic field.

C-13 Spin Diffusion at Natural Abundance

The fact that C-13 nuclei are only 1.1% abundant makes the most probable distance between C-13 nuclei in a polymer of the order of 0.7-0.8nm. At such distances, C-13 spin exchange due to the C-13 dipolar interaction is a slow process and its inefficiency is also attributable to the existence of possibly strong C-13-proton dipolar interactions. However, given a crystal polymer with intrinsically long longitudinal relaxation times (>100s) C-13 spin diffusion becomes an important tool for probing the environment around a given carbon over distance of 0.5 to 0.8 nm (one or two intermolecular distances).

C-13 spin diffusion studies of polyethylene have demonstrated the slow, temperature-dependent relative motion of the two chains within the unit cell. A similar study on cellulose has demonstrated crystalline polymorphy in certain native celluloses, particularly the algal celluloses. The latter finding may have some commercial implications because the rates of hydrolysis in strong acid also seem to be different for the two crystalline forms.

Vibrational Spectra of Crystallographic Defects

Short chains of polyethylene in a crystal tend to move as rigid rods, particularly by rotating around or translating along their long axes. However, as the chains become longer, the misfit energy associated with rotation or translation as rigid rods increases with the chain length. Above a certain length, it becomes energetically favorable for the polymer to create a localized defect, consisting of a short sequence of dramatically changed conformations which permits the undistorted parts of the chain to fit into the crystal lattice. For polyethylene, this transition occurs when the chain reaches a length of around 30 carbon atoms.

Minimum energy conformations of these defects were calculated using interatomic potential functions. Although defects can be modeled in short chains, end effects are troublesome. The new supercomputer at NBS enables calculations to be made in reasonably short times on longer chain segments so that end effects are minimized. The minimum energy conformation and the vibrational spectra of defects in chains containing up to 44 carbon atoms can now be calculated in a matter of minutes. Periodic boundary conditions were used to eliminate singularities at chain ends. These boundary conditions create a long chain with a repeat unit as long as the original chain. This repeat unit consists of a defect and a zigzag segment. The zigzag segment tends to vibrate like an n-alkane having the length of the segment. The limitations of a short segment are important for some modes, particularly the low frequency acoustic modes for which the frequencies depend strongly on the length of the vibrating segment.

Calculations of conformation and vibrational spectra were performed for dispiration, dislocation, and disclination loops surrounding a single chain, and for the partial disclination array known as a twist boundary. These crystallographic defects or boundaries play important roles in determining the physical properties of polyethylene and other polymers. In addition, similar calculations were performed for adjacent reentry folds in (110) and (200) planes.

Infrared and Raman intensities were calculated for all modes using the eigenvectors, a bond moment approach. The variations of the bond dipole moments were expressed in terms of the set of electro-optical parameters. For Raman intensities the electro-optical parameters are collected into separate matrices of bond mean polarizability derivatives and bond anisotropy derivatives. The elements of the polarizability tensor for each methylene group in the defect-containing molecular chain were calculated. The mean polarizability and the anisotropy of each CH_2 chain were also calculated. The resulting computer program can be applied to compare the observed and calculated Raman intensities of stretch oriented, defect-containing polyethylene, and also for Raman spectra of polyethylene powders.

The interpretation of the vibrational spectra is greatly facilitated not only by the increased chain length that can be handled in the new NBS computer, but also by the refinements in the graphical methods for displaying the displacements and infrared intensities of each CH_2 group. The molecular graphics made features of the following sort visible and clear. Some of the modes introduced by the presence of a defect derive entirely from the motions of atoms in or very close to the defect. The frequencies of these modes lie at values not encompassed by any part of the dispersion curves for vibrations of the polyethylene lattice. Little coupling of these defect vibrations with the lattice vibrations is observed. The observed 680 cm^{-1} band is of this nature, as this frequency is outside the range of the dispersion curve for the rocking mode of the polyethylene lattice. It was found to be associated with a gentle twist of the polyethylene chains which occurs at twist boundaries. This band is relatively intense in rapidly quenched samples. It was suggested that twist is the basic morphological feature that results in the long period observed in polyethylene fibers. Reports in the literature of an absorption band at 680 cm^{-1} indicates that twist is present and provides support for this suggestion. Other modes found near 1421 cm^{-1} are also identified with defect vibrations not coupled to lattice vibrations.

Vibrational modes associated with defects at frequencies that lie within the ranges encompassed by the dispersion curves of the crystal generally are strongly coupled to the lattice vibrations. In the absence of the defect these lattice modes are not infrared active, but the presence of the defect provides coupling between the light waves and the molecular vibrations. There are many such modes in polyethylene containing defects. Defect and crystal parts of the chain may vibrate in a way that both regions contribute to the absorption intensity or, if the vector sum of their motions tends to cancel, the absorption may be weaker than it would be for an isolated oligomer fixed in the defect conformation. These defect coupled modes are so closely spaced and so weak that it is unlikely that many of them can be resolved experimentally. The observed effect of such defect vibrations is to contribute to the broad background absorption commonly observed in polyethylene.

The modes which are clearly associated with the defects are governed primarily by the dihedral angles associated with about three successive bonds. A band near 750 cm^{-1} is associated with gauche-trans-gauche sequences. A band near 1420 cm^{-1} is associated with a different sequence of trans and gauche dihedral angles. The band at 680 cm^{-1} is an exception to this rule, since it is associated with a longer sequence of dihedral angles (about 9) which all differ from trans by less than 25°.

Techniques for Handling Single Molecules and Small Fibers

To examine single molecules at very high resolution in an electron microscope or in the new scanning tunneling microscopes, it is desirable that the molecules be extended and attached to a conducting substrate. Techniques were developed to disperse single polymer molecules or thin fibers containing from a single molecule to a few tens of molecules in a reasonably dense pattern that extended over a large area. Examination of such samples is expected to reveal molecular features such as chain branching and the distribution of comonomer units along a copolymer chain. Since it is now possible to make computer models of structural features such as twist boundaries in fibers containing a few tens of polymer molecules, it may also be possible to compare observed and calculated morphological features.

A variety of methods for preparing molecular scale polymer samples on cleaved mica surfaces from which the molecules can be transferred to the electron microscope or to a scanning tunneling microscope were investigated. These include spreading a dilute polymer solution on cleaved mica or trapping the solution between freshly cleaved mica surfaces. Wiping solid polymer particles or partly dissolved polymer across a mica surface was found to leave fibers which tapered to molecular dimensions. Thin layers of very lightly crosslinked gel trapped between mica layers offer another class of routes to polymer networks with the properties sought.

These procedures are being developed using observations of platinum carbon shadowed samples in the transmission microscope as a guide. Single molecule particles, particles or crystals containing many molecules, fibers, fibers with crystal overgrowths (shish-kebabs) and folded chain crystals with fibers drawn out of them have been prepared. the major effort is on polyethylene since its morphological features are familiar. PBT (poly-p-phenylene-benzbisthiazole) and poly-gamma-benzyl-glutamata were examined because they are expected to be rodlike, but no rodlike single molecules have yet been observed, probably because of the limits on resolution imposed by the platinum-carbon shadowing technique. Gelatin and polyacrylamide crosslinked networks were investigated. the resolution limits of the electron microscope methods set a lower limit on the size of the finest fibers observed.

The smallest fibers seen in the electron microscope contain 30 or more polymer molecules. This is already a small enough number to be commensurate with the ensembles of molecules used in the computer modeling of twist boundaries in polyethylene and other crystalline defects. The fibers that we have already produced and observed in the transmission microscope are of a suitable size for the observation of some of the features modelled in the computer, particularly the twist boundary. Development of the electron microscope and electron diffraction procedures for observing the long period in small polyethylene fibers is underway. Techniques for observing polymer molecules in the scanning tunneling microscope are being developed in cooperation with groups at NBS and IBM San Jose, who are building scanning tunneling microscopes. Practical scanning tunneling techniques for observing the structure of single molecules will make it possible to observe features such as branching, block copolymerization, and network architecture. These aspects of the molecular structure of polymers are not directly observable at present and must be deduced, more or less reliably from the chemical history of the sample, NMR measurements of short chemical sequences, end group analysis, swelling measurements, or the like. The availability of a direct way of observing the structure and connectivity of single polymer molecules will be extremely valuable in the characterization of copolymers used in polymer blends, biological molecules such as DNA or proteins, networks in rubbers, or in the matrices of reinforced composites.

Looking further to the future, the ability to combine inelastic tunneling spectroscopy with scanning tunneling microscopy would permit an elegantly incisive analysis of the structure of very complex molecules. Also, the ability of scanning tunneling microscopy to observe the spatial variation of the work function and related electronic parameters will make possible the observation of parameters needed to incorporate molecules into useful electron devices.

Differences in the Molecular Weight and the Temperature Dependences of Self Diffusion and Zero Shear Viscosity in Linear Polyethylene and Hydrogenated Polybutadiene

Within the context of a general coupling model we can support the hypothesis that while the modes of relaxation for self-diffusion (D) and shear flow (η) are the same, the entanglement interactions are different. We assume that there are two distinct coupling parameters n_D and n_η for D and η respectively. The model predicts the molecular weight, M, and temperature (T) dependences to be scaled by the relevant coupling parameters as: $\eta \propto [M^2 \exp(E_a/RT)]^{1/(1-n_\eta)}$ and $D \propto [M^2 \exp(E_a/RT)^{-1/(1-n_D)}$ for melts with Arrhenius temperature-dependence. In these relationships, E_a is the activation energy. We have found that n_η=0.43 and 0.42 for polyethylene, PE, and hydrogenated polybutadene, HPB, which scale η as $M^{3.5}$ and $M^{3.4}$. Also, the respective apparent flow activation energy E_η^* of 6.35 and 7.2 kcal/mole scale to primitive activation energies of 3.6 and 4.2 kcal/mole. On the other hand, the M^{-2} dependence of D results in n_D = 1/3. The reported activation energies for self-diffusion in PE and HPB of 5.49 and 6.2 kcal/mole scale to primitive activation energy E_a's of 3.7 and 4.1 kcal/mole, respectively.

A Comparison of the Linear Viscoelastic Behavior of Cyclic and Linear Polystyrenes in the Melt

This study is part of an ongoing collaboration between several laboratories to study the molecular rheology of cyclic polymers. In the past year we have carried out studies of the recoverable compliance and zero shear viscosities of a series of cyclic polystyrenes having a range of molecular weights from 19,400 to 390,000 g-mole.

This study used samples made at the Centre de Recherches sur les Macromolecules in Strasborg and at the University of Akron (by Hostetter and Fetters). As found previously [1], the zero shear viscosity of the cyclic polystyrenes is virtually the same as that of the linear materials above some critical molecular weight for entanglement, M_c. Our recent results further substantiate the finding that $\eta_o \; \alpha \; M^{3.4}$ for the cyclic molecules as is the case for the linear molecules. Furthermore, the critical molecular weight for entanglement coupling, M_c, from viscosity measurements is found to be the same for both the cyclic and linear molecules, i.e., M_c~32000.

On the other hand, the recoverable compliance of the cyclic and linear molecules is found to differ significantly. The plateau compliance, J_N^0, for the cyclic molecules is found to be twice that for the linear molecules, indicating that the molecular weight between entanglement points for the cyclic polystyrene is twice that of the linear polystyrene. Furthermore, it is found that the steady-state recoverable compliance, J_e^0, for the cycles is twice J_e^0 for the linear chains. Therefore, the breadth of the relaxation spectrum $J_e^0/J_N^0 \approx 2.5$ is the same for both the cyclic and linear systems.

1. G. B. McKenna, G. Hadziioannou, P. Lutz, G. Hild, C. Strazielle, P. Rempp and A. J. Kovacs, "The Molecular Weight Dependence of the Zero Shear Viscosity of Cyclic Polystyrene Molecules in the Melt", to be published.

A Model for the Calculation of the Degree of Non-Adjacent Re-Entry in Crystal Growth

A simplified model for the calculation of the degree of non-adjacent re-entry may be developed and solved using previously developed theoretical methods [1]. At the end of a strip growing on the lateral edge of a lamella, three processes are viewed as occurring: (1) the polymer chain at the terminal end of the growing strip may fold to make an adjacent re-entry fold; (2) a dangling cilium further back in the strip may fold onto the growing end to form a non-adjacent re-entry fold; (3) a new chain from the supernatant may be incorporated at the end of the strip. While in principle this model may be solved for the folding of a chain to form a non-adjacent re-entry from any location behind the terminal one, mathematical tractability has so far limited solution only to the case where non-adjacent re-entry occurs from the penultimate location in the growing strip. In that case, the configuration at the terminal two positions may be considered "species" in the sense of the previous theory [1]. For the case of n-paraffin crystals with a lamallar thickness that is just half the length of the extended chain (i.e., a single fold in the chain), this leads to a 6x6 transition matrix with only eleven non-zero elements, while for a polymer chain, the corresponding matrix is 8x8 with 21 non-zero elements.

The "composition" of the chain may determined using previous methods. Preliminary results for different under coolings, ΔT, are as follows for n-paraffins and polyethylene at a concentration of 0.01%:

	n-Paraffin		Polymer	
	ΔT=20	ΔT=16	ΔT=20	$\Delta T\overset{*}{=}0$
% Adjacent	99.6	96.2	89	46.45
% Non-adjacent	0.31	3.72	7	46.45
% Cilia	0.03	0.06	4	7.1

*at equilibrium

The undercooling is from the melting point of the extended chain crystal.

The amount of non-adjacent re-entry increases with solution concentration and with decreasing undercooling. These preliminary results will be refined and extended to other cases.

[1] J. I. Lauritzen, Jr., E. A. DiMarzio, and E. Passaglia, J. Chem. Phys. 45, 4444 (1966).

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

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 polymers 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, J. M. Guenet of Centre de Recherches sur les Macromolecules, Strasburg, France, has made a comprehensive experimental study of the SANS of isotactic 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.

The Lateral Growth Habits and Sectored Character of Polyethylene Crystals

Previous studies [1] of the habits of lamellar (chain-folded) crystals of polyethylene fractions (M.W, 10^4-10^5) grown from relatively poor solvents (heptyl acetate and dodecanol) in the range 95°C-120°C revealed, inter alia, the following features concerning their aspect ratio R (length parallel to $\underline{b}$-axis/length parallel to $\underline{a}$-axis). For the same solvent, R was larger the higher the growth temperature, it was also larger at a given growth temperature the lower the molecular weight. For the same molecular weight and growth temperature the aspect ratio was larger for crystals grown from heptyl acetate than from dodecanol (which is the poorer solvent). Overall R ranged from 1.8-6. The crystals are bounded laterally by {100} and (200) faces along which growth occurs through the accretion of chains in a folded conformation. The usefulness of these crystals as models for the constituent lamellae in polyethylene spherulites grown from the molten state has been pointed out [1]. A feature of interest and puzzlement concerning these crystals is that the longer lateral sides [(200) faces] tend to exhibit more pronouncedly curved profiles, the higher the growth temperature (and correspondingly the larger the aspect ratio) [1]). This trend raises some questions concerning the details of the mechanism of lateral growth of the crystals and, correspondingly, the nature of the sectored character of the crystals. This latter aspect is currently being investigated. Earlier observations derived from an examination of the diffraction contrast characteristics of the various crystals are being complemented by the application of the recently developed surface decoration technique of Wittman and Lotz [2]. Examination of decorated crystals with aspect ratios R=2.5-4.5 in the transmission electron microscope revealed the following: (1) The crystals are six-sectored, (2) the boundary between adjacent {110} sectors is sharp in all the crystals, (3) the boundary between a {110} and an adjoining {200} sector, although sharp in crystals with aspect ratio 2.5, becomes progressively more diffuse the larger the aspect ratio. This trend may be associated with distortions in the conformations of the crystals resulting from the accommodation (in the sector boundary region) of differences in the tilt of the stems relative to the fold surface in the {110} as compared to that in adjacent the {200} sector. This speculation and its possible relevance in connection with the increasingly curved character of the longer faces of the lamellae the higher their aspect ratio are being delved into.

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Mechanical Properties Measurement and Modeling

Subtask 2 of Task 14336

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

The effects of thermal history on the volume of polymer glasses is well known, and the physics of volume changes are reasonably well understood. However, the impact of this so-called "physical aging" on the properties of the polymers in the nonlinear viscoelastic range and near failure are not well understood. Furthermore, the coupling between large mechanical excitations and the volume recovery of the glasses is not at all understood. The ongoing efforts to elucidate the physical and mechanical aging behavior of polymers are described.

The characterization of the response of polyethylene, a semicrystalline polymer, to small deformations has lead to an advancement of our understandiang of visco-plastic performance. The surprising necessity of using a nonlinear constitutive law, even at small deformations, to accurately describe the long-term creep behavior of this ubiquitious polymer has been described.

The mechanical behavior of elastomers is a subject of both theoretical and practical interest. Research is present which deals with the use of continuum physics to relate to molecular theory of the behavior of polymers in the rubbery state and to understand an anamoly discovered in the behavior of natural rubber at extremely small deformations.

The mechanical behavior of physical gels has heretofore been treated within the context of rubbery like behavior. Evidence suggesting that this is not the case has been obtained from careful measurements of the solvent and concentration dependences of the compressive properties of isotactic polystyrene gels. Such results impact our understanding of gel formation and the mechanical properties which result.

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

Effects of Physical Aging on the Creep Rupture Behavior of Poly(methyl methacrylate)

Upon isobaric cooling through their glass transition range, under-cooled liquids, including polymers, are known to depart from their thermodynamic equilibrium. The resulting non-equilibrium glasses are intrinsically unstable and evolve spontaneously towards their equilibrium structure. The approach towards structural equilibrium is reflected by the time dependence of the volume and enthalpy of the glass. The changes in viscoelastic properties associated with the evolving structure of the glass has come to be known as physical aging [1].

The extensive work of Struik [1], suggested that aging can be described by merely shifting the retardation spectrum of the glass towards longer times. Furthermore, in the linear viscoelastic range, the value of the double logarithmic shift rate:

$$\mu = d \log \underline{a} / d \log t_e \qquad (1)$$

is close to unity in a rather wide temperature interval below the glass transition temperature Tg. Log $\underline{a}$ denotes here the shift along the logarithmic creep time, t, axis to superpose the creep compliance, $J(t,t_e)$, curves determined at increasing values of the t_e, the aging time or time after quenching from above T_g to the aging temperature.

The effect of large stresses or deformations on the aging behavior of the glass have been also investigated [1,2] with the finding that the shift rate, μ (see equation 1) decreases with increasing stress or deformation. Little work has been carried out, however, to examine the effects of physical aging on the time-dependent failure behavior of polymer glasses. This study addresses specifically this issue.

Samples of a commercial grade poly(methyl methacrylate) (PMMA) were machined into the shape of ASTM type dumbbell specimens, placed between glass plates and heated to 120°C (where T_g for PMMA≈110°C) for 1 hour. The samples were subsequently removed from the 120°C oven and placed in an oven at 80°C where they were aged for times ranging from 10 min. to 250 days. The samples were removed from the 80°C oven, left at 23°C for one week, and then tested in creep at large stresses. Creep deformation measurements were taken using a cathetometer to read the distance between gage marks placed at the center of the sample. Time to rupture was recorded for each sample.

There are two salient features which result from the preliminary analysis of the data obtained to date:

1) Aging of the glass as measured by the increased creep compliance with aging times continues for the full duration of the testing, i.e., 250 days of aging.

2) At aging times of less than 10 days (at 80°C) the lifetime of the glass increases with increasing aging times, while after 10 days of aging the time-to-failure is independent of aging time.

Further work is underway to understand why the creep and creep rupture behavior are not affected in the same way by the changes in glassy structure associated with the physical aging of the glass.

1. L. C. E. Struik, Physical Aging in Amorphous Polymers and Other Materials, Elsevier, Amsterdam (1978).

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Mechanically Induced Physical Aging and Nonlinear Viscoelasticity-Examples for Polymer Solutions and Glasses

There are several recent [1,2] reports of using small deformations superimposed on large deformations as a probe of molecular relaxation in polymer glasses. Although the experiments themselves are quite interesting, we find the use of linear viscoelasticity theory to interpret the incremental response to be ambiguous, 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 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 was to show that, although there may be structural changes associated with mechanical deformations of polymer glasses, the superposition of small strains on large as a probe of such changes is ambiguous. We show this by carrying out experiments on a material which undergoes no structural change (a concentrated solution of polyisobutylene (PIB) in a hydrocarbon oil) 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 $\Delta G(t)$ 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 10% of the predicted responses at shear deformations as large as 9.5. This result demonstrates 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 measurements are called for.

In a PMMA glass the incremental response is found to behave in a qualitatively similar way as it does in a polymer solution, i.e. $\Delta G(t)$ is smaller than $G(t)$ and increases with increasing time, t_e, after imposition of the large deformation. However, the BKZ theory predicts the effects to be much greater than what is actually observed. This indicates that the glass, if measured relative to the BKZ prediction, is hardening rather than softening, as found using the conventional interpretation relative to the linear response.

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Creep and Recovery Behavior of Polyethylene Under Small Uniaxial Deformations

It has been shown in previous work [1-2] that the creep and recovery behavior of an ultra high molecular weight polyethylene (UHMWPE), in the region of small uniaxial deformations, can be described quite well with a one-dimensional equation consisting of two terms, one a single integral hereditary term, and the other a plasticity term. This equation describes plasto-viscoelasticity. It was found that, for creep times of up to about 4×10^4 seconds, the contribution of the plasticity term at 23 °C was proportional to $t_1^{1/3}$, where t_1 is the time under creep. For creep times greater than 4×10^4 seconds the plasticity term became constant and independent of the time under creep. The plateau value was further found to be independent of temperature, at least up to a temperature of 57 °C.

This work has now been extended to two other polyethylenes, one a linear high density polyethylene, and the other an ethylene-hexene copolymer. Data were obtained at temperatures in the range from 23°C to 57°C and creep times of from 10 seconds to 4.3×10^5 seconds. In order to approximate constant true stress conditions all of the creep experiments were carried out at the same value of applied stress (4 MPa) and the change in strain during creep was in all cases less than 2 percent. Comparison of the present results with those from the earlier work on the UHMWPE shows that there is a great deal of similarity in the behavior of all three materials. The occurrence of nonrecoverable creep, or "plasticity", is a phenomenon general to polyethylene, and its dependence on temperature or duration of creep is very similar for all three materials. The behavior of the "plasticity" term has several features in common to all three materials: (1) The initial slope decreases with increased temperature. (2) The time at which the plasticity term reaches a constant value shifts to earlier times with increased temperature and the shift occurs in the same manner for all three polymers. (3) For a given material, the plateau value is essentially independent of the temperature. (4) The magnitude of the plateau value increases with decreasing density.

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The Mechanical and Swelling Behavior of Well-Characterized Polybutadiene Networks

There has been considerable renewed interest in rubber elasticity theory recently due to the success of the junction constraint model of Flory [1,2]. In this work, we have carried out mechanical and swelling measurements on well characterized polybutadiene networks and compared the results with the junction constraint model in a new way. To do this we use the concept from continuum mechanics of the Valanis-Landel (VL) [3] strain energy density function, i.e., a function in the principal stretches which can be represented as a separable sum of one function evaluated at each of the three principal stretches. We have further derived the V-L function for the junction constraint model of Flory, and compare it with the experimental data.

There are two salient results from our work: (1) while the Flory model fits the data extremely well, the parameters related to the network topology are not in particularly good agreement with those calculated from the chemistry involved in making the networks and (2) the assumption that the elastic free energy of deformation is equal to the free energy of mixing at swelling equilibrium can only be supported if one includes a logarithmic term in the strain energy function. The sign of this term is found to be opposite that postulated by Flory [1].

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Measurements of the Strain-Energy Density Function of Peroxide Crosslinked Natural Rubber at Small Strains

In two recent articles [1,2], we described experiments in which the torsion behavior and the tension-compression behavior of peroxide crosslinked natural rubber was examined at smaller deformations than had been previously reported. In this paper we present new results in which a sample of peroxide cured natural rubber was tested in torsion where both torque and normal thrust were measured. In this study the strains, γ, at which the normal force was measured were lower by a factor of 4 than those which we reported previously (γ=.0046).

As before we determined the derivatives $\partial W/\partial I_1$ and $\partial W/\partial I_2$ of the strain energy density function W with respect to the invariants I_1 and I_2, and have further confirmed the result from the prior study that for the peroxide cured rubber systems which are freshly prepared in our laboratory, $\partial W/\partial I_2$ does not become negative, even at extremely small deformations. These results are contrary to results reported in the literature by other measurement techniques [3,4] or with samples undergoing a different crosslinking (curing) history [5,6].

We further calculate the extension and compression behavior from the torsion data by determining the Valanis-Landel [7] function for the rubber using the method of Kearsley and Zapas [6] and compare them with the measured response. We find that the torsional data at small deformations do not predict the anomaly [2] of a cusp in the tension-compression moduli beginning at strains of $\varepsilon \approx 2 \times 10^{-3}$. Furthermore, the character of the reduced stress ($\approx E/3$) measured at small deformations is different from that calculated from the V-L function and torque/thrust data. This suggests that the V-L function is not a correct representation of the rubber's tension-compression behavior at low deformations. Kearsley [8] has suggested that this is due to compressibility effects in the rubber at extremely small extensions and compressions.

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Mechanical Properties of Isotactic Polystyrene Physical Gels

Isotactic polystyrene (IPS), solutions in cis-decalin, trans-decalin and chlorodecane, when quenched to low temperatures form physical gels. The mechanism of gel formation and the resulting structure of the gel is still controversial. In this study we examined the effects of solvent and polymer concentration on the room temperature compressive behavior of IPS gels formed at -20°C. There are three important results which appear from a preliminary analysis of the data which indicate that the gels do not exhibit classical rubbery behavior as would chemically crosslinked gels.

1. The gels show a definite viscoelastic response over the range 10 seconds to 3600 seconds. The relaxation rate tends to accelerate with time and the double logarithmic rate of stress relaxation, $d \log \sigma / d \log t$, is of the order 0.1 (It varies with time and solvent) which is much greater than observed in crosslinked rubber (~0.02).

2. The isochronal modulus at 120S does not follow a scaling type behavior. Rather the modulus-concentration dependence shows sharp features reminiscent of a phase diagram over narrow concentration ranges. The position of the sharp breaks in the modulus-concentration plots are dependent upon the solvent system.

3. In the cis- and trans-decalin gels, the amount of the solvent loss is independent of deformation and can be attributed to evaporation (~1.8% for cis- and 3.6% for trans-decalin). The chlorodecane gels show a solvent loss which increases with increasing deformation.

Work is ongoing to understand and extend the results obtained so far.

Mechanical Durability of Polymeric Materials

Subtask 3 of Task 14336

J. D. Barnes, G. W. Bullman, J. M. Crissman, B. M. Fanconi, K. M. Flynn, F. A. Khoury, G. B. McKenna

The objectives of Subtask 3 are to develop measurement methods and models of long term mechanical performance and to conduct joint projects with other government agencies on mechanical durability issues of concern to those agencies. Joint activities with other agencies provide opportunities to evaluate various approaches to mechanical durability on materials with known performance histories. The premature failure of polyethylene balloons used to lift scientific payloads for stratospheric research has been a concern to NASA. A joint project has been established to identify molecular and structural aspects of the PE film that impact performance.

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

A Comparative Study of the Structure and Mechanical Properties of Polyethylene Films Used in Heavy-Lift Balloons

This project is sponsored by the Balloon Projects Branch of the National Aeronautics and Space Administration (NASA). It is part of a broader ongoing investigation undertaken by NASA to determine the causes of catastrophic failures of helium filled heavy-lift balloons. These balloons whose capacity at float altitude can be as large as 50×10^6 cu.ft. are used to raise instrument payloads of up to 11,500 lbs to elevations of 100,000-150,000 ft. for various research projects. The helium is contained by proprietary low density polyethylene film (crystallinity 46.2-48.2%, [1]) which is 0.5-1 mil. thick.

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 onwards have been elusive. Among the possibilities which are being pursued by NASA is that there have been substantial changes in the proprietary polyethylene films used prior to and since 1980. The purpose of this project is to help establish a basis for determining whether poorer balloon performances are associated with differences in the fine structure and the mechanical characteristics of the proprietary films. Accordingly, various aspects of the structure and mechanical properties of films manufactured at different periods, including one produced prior to 1980, were probed in an exploratory study [1]. The work described below on four films (I, III, B1, F1) is a sequel to that earlier study. Films I and B1 are currently used in heavy lift balloons, whereas film III is representative of films used prior to 1980. Film F1 has as yet not been used in heavy-lift balloons.

Wide angle and small angle X-ray diffraction have been used to compare the orientation characteristics of the crystalline regions in the films and to probe the nature of their fine textures. The (200), (020) and {110} pole figures of the four films were determined, and small angle X-ray diffraction patterns were recorded with the X-ray beam parallel to each of the following directions: machine (M), transverse (T), and normal (N). While the results confirmed the following similarities between films I, III and B1 [1], film B1 differed in some respects from films I and III as will be indicated later. In these three films: (1) the a-axis is preferentially oriented in the MT plane, and preferentially parallel to M in that plane; (2) the b-axis is preferentially oriented in the NT plane and preferentially oriented parallel to N in that plane.

The features outlined above coupled with the small angle X-ray diffraction patterns exhibited by the three films can be interpreted in terms of an idealized working model in which it is envisaged that the films consist mainly of two populations of twisted lamellar microcrystals: a "transcrystalline" population and a "row-structured" population. The lamellae in the transcrystalline population are oriented with their b-axis parallel to N, with the a and c axes randomly oriented parallel to the MT plane. The occurrence of "row-structures" in polymer films has been discussed in detail by Keller and Machin [2]. The overall orientation characteristics associated with this type of lamellar texture in polyethylene are (1) the b-axis is oriented parallel to the NT plane and randomized in that plane, and (2) averaged over all the lamellae, there is a preferential orientation of both the a and c axes parallel to M. Comparison of the pole figures and small angle diffraction patterns exhibited by the three films indicate that the B1 film contains a smaller proportion of the "row-structure" population than films I and III.

The F1 film was found to differ distinctly from films I, III and B1. Both the pole figure data and the small angle X-ray data indicated that the texture was predominantly of the "row-structure" type. There was no evidence of a transcrystalline type of population.

In the area of mechanical deformation, the biaxial (bubble geometry) deformation behavior of the films under inflation was examined at both 23°C and -73°C. In the region of the pole of the bubble it was found that films I and B1 both deformed by almost equal amounts in both the M and T directions with no evidence of necking even up to the point of failure indicating that the films are relatively "well balanced". On the other hand, films III and F1 exhibited necking in the T direction and as a result deformed significantly more in that direction than in the M direction. Film III exhibited multiple necking, whereas only one necked region occurred in the F1 film. The results of the elongation to break experiments in uniaxial extension at 23°C obtained earlier [1] for films I, III and B1, and more recently for film F1 are consistent with the behavior of the films under biaxial deformation. The imbalance in the deformation in the T relative to the M direction exhibited by the F1 film is consistent with the distinct difference indicated above between its fine structure and those of the other three films. Correspondingly, it has also been found that the shrinkage behavior in the M relative to the T direction exhibited by the F1 film differed distinctly from the behavior of the other three films. Thus, F1 shrank by a factor of about twelve in the M direction and expanded by a factor of 1.35 in the T direction. In contrast, films I, III, and B1 shrank in both the M and the T directions. The shrinkage factors for these three films were as follow: Film I:4.29 (M), 2.84(T), ratio 1.51; film III:4.69 (M), 2.51(T), ratio 1.87; film B1: 4.22(M), 3.11(T), ratio 1.36. The corresponding ratio of the strain-to-failure in the machine to the transverse directions for the three films were: Film I:0.98; Film III:1.40; film B1:0.96. No clear-cut correlations between differences in the balance of mechanical properties in the M relative to the T direction, the shrinkage behavior, or the orientation characteristics of films I, III and B1 (whose crystallinities are very nearly equal, 46.4%-48.2%, see Ref.[1]) have emerged from the experiments described above. It may be noted in this connection that the shrinkage ratio in the M relative to the T direction for the B1 film (which apparently contains less of the "row-structure" type of texture) is 1.35 as compared to 1.51 for film I, whereas the ratio of the strain to break in the M relative to the T direction at 23°C is essentially the same for both films.

It was established in our earlier study that the degree of branching in the constituent polymer chains in films I, III and B1 was the same (2 methyl groups/100 carbon atoms [1]). Analysis of gel permeation chromatograms showed however that on a relative basis the polymer in film III had the highest average molecular weight (M_w) followed in decreasing order by films I and B1. In the case of film F1, the chains have been found to be less branched (0.5 methyl groups/100 carbon atoms. The molecular weight characteristics and crystallinity of this film are currently being determined. The influence of the differences in molecular weight on the observed mechanical properties of films I, III and B1 remains an open question.

In summary, although differences in either molecular weight, fine texture, or mechanical properties have been identified between films I, III and B1 (which have been used in heavy-lift balloons) it remains unclear why these differences should lead to the failure of one type of film and not another in the "balloon environment". The question of ductility arises. All of the tests employed in this study indicate that all three films retain considerable ductility at -73°C. One aspect not addressed in this study however is that of high-velocity impact. All of the measurement methods used involved rates of deformation which are relatively low. For example, the rate of strain in uniaxial tensile measurements was 991%/min [1]. As the balloon ascends through the region of lowest temperature in the troposphere, it is observed that folds in the balloon pop out at a high velocity. If this velocity is sufficiently high the behavior of the polymer will become more glass-like and the ductile to brittle characteristics of the films may change. This is an area where differences in molecular weight or molecular weight distribution may become critical factors. This possibility bears examining more closely.

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Mechanical Durability of Rubber Compounds for Tank Track Pad Applications

Failure behavior of a carbon-black filled rubber (15TP-14AX, MIL-T-11891) is being studied under uniaxial tensile testing conditions. Static and dynamic (fatigue) testing have been performed to study the material behavior within the context of a cycle shifted failure envelope model of rubber rupture. Results from testing of a standard filled butyl rubber formulation are presented for comparison. Our results show that the behavior of the 15TP-14AX rubber, while showing a greater lifetime than that of the butyl rubber, is qualitatively similar. Failure times for both rubbers decrease with increasing test frequency. Importantly, the number of cycles to failure increases with increasing test frequency.

The failure lifetime of the rubbers can be related to the stress softening behavior under cyclic loading conditions. If it is assumed that, in some sense, a failure envelope exists, then it can be shown that under cyclic loading the filled rubbers (which stress soften) should fail at a time earlier than under constant loading conditions. We have been able to predict failure lifetimes by using creep data obtained from short-time cyclic loading extrapolated to the shifted failure envelope. This approach relates the observed frequency dependence of lifetimes to the creep behavior under cyclic loading conditions.

PROCESSING AND RELIABILITY OF POLYMER COMPOSITES

Task 14337

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

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

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

To assist in conducting this broadly based effort, the Task is utilizing a number of cooperative programs as well as the the assistance of experts who, in some cases, have spent time working in the Division during the last year. A major new aspect of this cooperation was the initiation of a Composites Colloquium Series which brought many world renown scientists to NBS for discussions. The cooperative efforts involve programs with NASA Langley Research Center, the Department of Treasury, and the industrial research laboratories at Hercules, Hexcel, and Texaco. In addition, joint programs were conducted with Drs. S. S. Wang at the Univ. of Illinois, A. J. Kinloch at Imperial College (London), and R. S. Stein at the Univ. of Massachusetts. Guest workers and visiting scientists during the last year have included Dr. H. Benoit from Centre de Recherches les Macromolecules in France and Mr. A. Gilet from the Ministry of Defense in Israel.

FY 85 Significant Accomplishments

- The previously developed theoretical basis for the characterization of the molecular network structure in thermosetting polymers was refined and applied to the analysis of neutron-scattering experiments. This analysis has successfully determined both the chemical and topological heterogeneities in a model epoxy. This represents the first time such important information could be obtained.

- The formation of a superlattice-type molecular network was discovered in certain epoxy systems. For these systems, cured with mixtures of crosslinking agents of different molecular weights, the chemical arrangement of the crosslinking molecules was found to be highly regular; the high and low molecular weight species incorporating themselves into the network in an alternating pattern. This was completely unexpected and experiments to determine why this happens and how if affects the properties are now underway.

- The high fracture energy of toughened polymers is of great importance for improved adhesives and composites. This high toughness has been shown to result from the development of a large crack-tip deformation zone. Scanning electron microscope studies have established yielding and plastic flow as the primary deformation mechanisms in this zone. A non-linear finite element analysis was successfully used to model the development and growth of this zone during fracture experiments.

- Delamination behavior was studied for six different thermoplastic composites, and where comparisons could be made, the interlaminar fracture energies relative to the toughness of the polymers themselves were lower than in comparable toughened thermoset composites. This less than optimal performance in such composites was attributed to the poor fiber-polymer bonding that was found in all but one case. This result has led to the initiation of new research programs at NBS, NASA, and numerous companies aimed at improving this bonding in thermoplastic composites

Cure Monitoring and Process Control for Polymers and Their Composites

Subtask 1 of Task 14337

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The changes that take place during the processing of a composite laminate are very complex, involving both chemistry and flow. As a result, no single technique can provide enough information to monitor all of the events that occur. Probably the most important cure feature is the change mechanical properties that takes place sinceit controls the consolidation of the composite and strongly influences the final properties of the laminate. Unfortunately, mechanical property measurements do not explain why the changes occur and are difficult to apply in actual production situations. Consequently, it is highly desirable not only to develop mechanical property testing techniques for laboratory specimens, but also to compare the results with those from other cure-monitoring techniques, particularly techniques that have on-line measurement capabilities.

In this subtask we are actively developing a variety of techniques based on the measurement of mechanical, electrical, optical, and thermal properties. Neutron-scattering techniques which are also being applied to the study of cure will be covered in a separate Subtask. A major strength in the program is the availability of a wide variety of new and established techniques. The goal is not only to develop new methods but also to apply a wide variety of techniques to the study of model systems so that a basic understanding can be developed and processing models can be formulated.

Mechanical Property Methods

Two measurement methods for mechanical properties are currently under development: an ultrasonic technique which has been described extensively in previous Annual Reports, and a torsional oscillation method similar to that under study in other laboratories. This second technique employs a ribbon of fabric that has been impregnated with the prepolymer. The mechanical properties of this coated fabric are monitored by small-amplitude torsional oscillation and followed as the polymerization cures. The effective elastic stiffness and the damping behavior are then determined as a function of cure. Frequencies between 30 Hz and 0.00003 Hz can be used.

To test this measurement method, initial experiments have been conducted using a model system consisting of a standard epoxy {(diglycidyl ether of bisphenol A, DGEBA)} and 2-ethyl-4-methylimidazole (EMI) as catalyst. Figure 1 shows the results for the elastic stiffness measured at a curing temperature of 60 C. As shown in this Figure, the elastic stiffness shows little change in the initial stages of cure, and then the stiffness increases rapidly before leveling off at a final value. The successful development of this test method means that comparison experiments can now be conducted with other cure monitoring techniques using this model system cured under identical conditions. Such experiments are now underway with viscosity and ultrasonic measurements as well as tests based on the electrical, optical, and thermal techniques described below.

Electrical Methods

The technique of dielectric spectroscopy has been shown to be an easily implemented method for monitoring the cure of composite resins, and it can easily be automated and incorporated into process control. In the initial stages of cure, however, the conductance often dominates the dielectric loss and is a more useful measurement. Consequently, the experiments performed here have monitored cure both with an automated, real-time AC conductivity measurement system for the early stages of cure and with the NBS dielectric spectrometer for the later stages of cure.

For the samples measured to date, the data have shown that AC conductivity at 50 Hz (which reflects to some extent the changes in viscosity) can be used to monitor the cure since conductance is the main feature for most of the cure cycle. Typical results are shown in Figure 2, which represents data for the model system (DGEBA-EMI).

An important problem in composite processing is the limited storage time for the starting materials, i.e., the fiber cloth or tape impregnated with the uncured resin. One of the storage effects is the very slow polymerization of the resin. If the cure state could be determined, the processing might be adjusted to compensate. To examine this idea, a partially cured resin sample was reheated and the polymerization taken to completion. A conductance curve was obtained for this sample and compared with the curve for a normally cured sample. It was found that the data for the partially cured resin was identical to the last part of the cure curve for the reference sample. This suggests that a conductance measurement could be used to monitor the initial cure state of the resin, both to estimate shelf-life and to determine the curing time needed for that batch of resin.

Optical Properties Methods

Two optical methods are under development for cure monitoring: Fourier transform infrared spectroscopy, which has been described in previous Annual Reports, and a fluorescence spectroscopy technique. The second method uses the sensitivity of the fluorescence intensity of some organic molecules to the local (molecular level) viscosity. Optical fibers are used to bring the excitation light into the interior of a curing composite component. Future work will seek to use the optical fiber to collect and transmit the emitted light out of the composite for detection as well. The light in the fiber excites probe molecules that are located within the penetration depth of the evanescent wave around the optical fiber. The penetration distance depends on the refractive indices of the waveguide and surrounding matrix, as well as the angle of incidence that the propagating light makes with the optical fiber-matrix interface. Thus, this approach is particularly sensitive to the interfacial region, and the proper control of this region is of critical importance for achieving desirable mechanical properties and performance in the composite.

Polymerization studies on amine-cured epoxy resins had shown that the excimer-type of fluorescence probe is sensitive to viscosity changes in the early stage of curing. Other probe molecules with fluorescence sensitivities over a wider viscosity range are now under investigation. Experiments are also being used to study the user of a second probe molecule, which has a viscosity insensitive fluorescence and can therefore be used as an internal reference. At the low concentrations, around 5×10^{-5}M or less, the probe molecules are not expected to have an effect on the resultant mechanical properties of the composite part.

A significant advantage of waveguide spectroscopy for composites is that the sampled material lies near the fiber-matrix interface, and by varying the penetration depth of the evanescent wave it may be possible to profile the viscosity distribution during chemical change in the interfacial region.

Thermal Property Methods

Differential scanning calorimetry (DSC) can be used to determine the amount of heat released during the cure reaction and thereby to measure the degree of cure or crosslinking. The reaction kinetics may be followed either isothermally or in scanning mode. The DSC can also be used to study the glass transition regions as a function of the degree of cure or as function of curing history.

Experiments using DSC to monitor cure have been successfully conducted with the model DGEBA-EMI system. Comparison studies are now underway using DSC in combination with other methods to monitor the same cure reactions and compare the results. Figures 1 and 2 show preliminary results for such tests with dynamic mechanical experiments and conductance measurements. The peak of the exothermic reaction in DSC occurs well before the drastic increase in the stiffness or the several decade reduction in the conductivity, even if some lag time is allowed for the samples to reach the oven temperature in the mechanical and the conductance measurements. Hence the mechanical and the dielectric measurements seem to be more sensitive to the later stages of cure. This is consistent with the idea that thermal measurements are sensitive to pregelation chemistry while the increase in elasticity and viscosity are associated with events near and after gelation.

Investigation of the Curing of Intaglio Inks

As an example of the practical application of cure monitoring, one project in this Task is employing various measurement and process monitoring techniques to follow the mixing and cure of intaglio inks. The objective in this work is to analyze the variability in these inks and identify the sources of this variability. To study the uniformity of the inks, a thermogravimetric ashing method was used to determine the percentage of non-combustible material in samples taken from various points within different ink batches. The degree to which the inks had cured during the mixing and milling associated with fabrication was followed by examining the tong oil component usingultraviolet (UV) absorption measurements andgel-permeation chromatography (GPC) determinations, which estimate relative molecular weight. Cure behavior was monitored with relative viscosity measurements on samples dried for various times in air on a rubber mill to simulate some of the conditions on a printing press.

Just as in the work previously described, the results here show that viscosity measurements are not sensitive to events that occur during the early stages of cure while GPC, for example, shows significant changes are taking place. This explains why viscosity measurements on uncured inks were not an effective quality control tool. The results also suggest a correlation sometimes exists between uniformity and cure behavior, and this means that inadequate mixing is a problem. A large data base on ink behavior has been generated and is now being analyzed to provide recommendations for reducing the variability and improving the quality on inks.

Analysis of Structure in Polymers and Their Composites

Subtask 2 of Task 14337

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The determination of structure in thermoset resins and their composites is a vital step in relating processing and formulation parameters to performance. During the past year, two new techniques have been developed to address this problem. The first involves the determination of morphology in phase separated systems and the second, which comprised the majority of effort during the last year, focused on network structure in epoxies.

Morphology in Phase Separated Resins

Phase separated systems such as rubber-modified epoxies are of great commercial importance because they are very tough. This toughness, however, is highly dependent on the morphology that is generated during processing and the relationships among formulation, processingand morphology are not known. Duringthepast year, a technique has been developed in cooperation with Dr. A. J. Kinloch at Imperial college to characterize the volume fraction and particle size distribution of the phase-separated component using transmission electron microscope pictures and an appropriate analysis. This method was applied to evaluate four formulations of rubber-modified epoxies having very different morphologies. The fracture behavior of these materials was also determined and evaluated using procedures developed previously to handle highly viscoelastic failure data. This represents the first time that detailed data on both morphology and properties have been obtained for such systems. Although the number of systems that have been analyzed so far is limited, this work is the beginning of a data base that will eventually establish clear structure-property relationships for these commercially important materials.

Molecular-Network Structures of Single-Phase Resins

The network structure of thermosetting resins used as composite matrix materials largely determines some of the key properties for composite materials. This structure refers to the arrangement of chemical crosslinks which converts the liquid monomers into a rigid solid. The network structure in these materials is not amenable to characterization by standard techniques such as small angle X-ray scattering, electron microscopy, nuclear magnetic resonance, etc. One of the major aspects characterizing the network structure within epoxies is the spatial distribution of the crosslinks. Studies in the Composites Task, however, have demonstrated that elastic neutron scattering has the unique potency for addressing this problem. Neutron measurements have been carried out successfully to characterize the molecular networks in one of the commonly used types of resins - i.e., the epoxies. A partially deuterated diglycidyl ether of Bisphenol A (DGEBA) and a curing agent based on polypropylene oxide chain were chosen as the model system for the study. The neutron scattering results can be analyzed by expressing the scattered intensities in terms of a form factor of an individual network of infinite molecular weight. Based on this formulation, the average size of the mesh and the rigidity of the network could be deduced from the scattering data. In addition, a decades-old controversy concerning the homogeneity of the networks within thermosets can now be treated analytically using this neutron technique. The heterogeneity in epoxies can be divided into two categories; the compositional fluctuation and the topological fluctuation. The compositional fluctuation of a network is defined as the variation in the chain length and the chemical composition among the linkages between crosslinks. This fluctuation can be related to the zero-angle (q=0) scattering intensity of a partially deuterated epoxy specimen through equation 1.

$$I(q=0) \propto \frac{\delta_1^2}{\langle n_1\rangle + \langle n_2\rangle}\phi_2^2 + \frac{\delta_2^2}{\langle n_1\rangle + \langle n_2\rangle}\phi_1^2 \qquad (1)$$

where δ_1 and δ_2 are the breadth of the molecular weight distribution in the epoxide and the amine linkages between the crosslinks, $<n_1>$ and $<n_2>$ are the average molecular weights, and ϕ_1 and ϕ_2 are the volume fractions occupied by these two species.

As to the topological variation within a molecular network, even for epoxies derived from an exclusive epoxide-amine reaction with monomers of a monodispersive molecular weight, contain topological variations such as tight loops, loose loops, and dangling ends as the inevitable consequence of the network formation. This type fluctuation will have an obvious effect on the swelling process of a bulk specimen and will result in a spacial variation of concentration for the swelling solvent. A neutron scattering experiment on solvent-swollen fully cured epoxies has been carried out, and the effect of the topological variation on the scattered intensities has been observed experimentally.

An analytic expression for scattering intensity of a swollen and topologically regular network with a compositional fluctuation has been derived. The zero-angle scattering intensity of such a swollen network follows the relation

$$I(q=0) = (1 - \frac{1}{SW})\,\phi_2^2 + \frac{1}{SW}\,\delta F_c^2 \qquad (2)$$

SW denotes the bulk swelling ratio and δF_c^2 denotes the right-hand term of equation 1. The difference between the observed scattering intensities and the one expressed by equation 2 can be taken as a measure of the topological heterogeneity.

For all the epoxies studied, the extent of chemical heterogeneity is quite low. The polydispersity between crosslinks , defined as the ratio of weight average to number average molecular weights, is less than 1.50. However, the epoxy networks are found to be highly irregular in terms of their topological connections. A program has been launched to elucidate the effect of these network heterogenities on the epoxy physical properties. The independent variables included in this ongoing program are the chemical composition of the monomers and the processing condition. In addition to the network structure parameters mentioned above, the fracture toughness (K_{ic}), glass transition temperature (T_g) , and degree of cure have been monitored in all the epoxy specimens included in this composition - processing study. In the following, an example of some preliminary findings in this program is described briefly.

Formation of Superlattice in Epoxy Network

In an effort to broaden the molecular weight distribution between crosslinks, Jeffamines of different molecular weight were blended together and cured with a stoichiometric amount of epoxy monomers. The molar ratio of the long chain amine (D-2000) to the short chain amines (D-400 to D-230) were kept at either 1.0 or 0.5. Each one of these cured mixtures gave rise to a pronounced scattering maximum at a q value smaller than those observed in the epoxy containing only one of the constituent amines. Theoretical consideration based on this experimental observation strongly suggested that the long chain and the short chain amines incorporated themselves within the epoxy network in a highly regular manner. The connecting linkage between a pair of short chain amines is a long chain amine and vice versa. Such a regularly alternating block structure within a amorphous material is rather striking. Work is now in progress to identify the mechanism of this regular network formation which can not be understood in terms of our current knowledge about epoxies.

Theglass transition temperature, T_g's, of the cured mixtures are always between those for samples made with either of the constituent amines alone. An example of results for one set of experiments is given in Table 1. The mixture containing one mole of D-400, one mole of D-230 and 4 mole of epoxy is of particular interest; the toughness of this material is far greater than that for either of the single-amine-cured samples. Experiments to study these systems in more detail are underway.

TABLE 1

Effect of Curing Process and Composition on Epoxy Properties

Composition	Curing Condition	Fracture Toughness ($10^{-6}N/m^{3/2}$)	T_g(°C)	Degree of Cure
DER332 (2) D-400 (1)	95°C/24 hrs.	1.14 ± 0.124	52	>95%
DER332 (2) D-230	100°C/24 hrs.	0.991 ± 0.026	91.4	>95%
DER332 (4) D-400 (1) D-230 (1)	100°C/24 hrs.	9.177 ± 3.037	70	>95%

Performance of Polymers and their Composites
Subtask 3 of Task 14337

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

Delamination

In recent years there has been a great deal of interest in composite delamination, i.e., the growth of cracks between layers of fibers either in the polymer that holds the fibers together or at the fiber-polymer interface. These cracks, which are thought to grow from impact damage substantially reduce themechanical performance of a composite, particularly in compression. The susceptibility of composites to this type of damage is attributable in part to the brittleness of the polymers normally used. To establish this connection at least for a simple type of fracture, a series of 23 different composites representing a wide range of resin types and fracture energies was examined. The mode-I fracture energies for bulk polymer samples were determined and compared with interlaminar fracture data on their composites. The results are shown in Figure 3, and the trends are in agreement with those reported last year based on preliminary results. The correlation can be qualitatively understood by noting that fiber breakage and pull-out increases the composite fracture energy while the constraint imposed by the fibers on the size of the crack-tip deformation zone lowers the composite fracture energy. The former effects are more important in brittle systems while the latter predominates with tough resins.

Thermoplastic composites are a particularly interesting case since their composites generally seem to exhibit a lower interlaminar fracture energies relative to their resin toughnesses than do comparable thermoset systems. Last year two thermoplastic composites were examined, and it was concluded that the lower interlaminar fracture energies resulted from poor fiber-matrix bonding. Four additional systems have now been studied, and similar results were found in all but one case. A new program to study interfacial bonding in thermoplastic composites is now underway.

Toughening Mechanisms

The generation of high fracture-energy polymer systems for adhesives and composites is a major industrial goal. To assist this effort, basic studies of toughening mechanisms are being conducted in this Task. A critical part of this work is the analysis of deformation mechanisms for various thermoplastic and toughened thermoset resins. Scanning electron microscope (SEM) pictures were taken of fracture surfaces in bulk resin samples and composites. Evidence of extensive yielding and plastic flow were found. This was confirmed by heating the samples above their T_g's for 10 minutes and then reexamining the same regions of the fracture surfaces. Substantial relaxation of the local deformations in the resin were found in both the bulk resin samples and their composites. For many of the tough systems, both the resin specimens and their composites exhibited stress whitening of the fracture in the initiation and slow crack growth regions. After the heat treatment, the original color was regained.

In an effort to model the toughening in such systems, high speed movies were made of the growth of the crack-tip deformation zone during loading. In cooperation with Prof. S. S. Wang at the Univ. of Illinois, a non-linear finite element analysis was conducted, and the results compared with data taken from the movies. The agreement was excellent. Future work will expand this analysis to include time-dependent effects since the failure behavior of these materials is known to be highly viscoelastic.

Adhesion

Adhesion plays an important role in the composites field. Numerous aspects of adhesion, both fundamental and applied, have been addressed in this Task. During the last year two particular topics were studied as part of an applied project. The project concerned the bonding of a highly filled composite to glass, and the durability of this bond when subjected to moisture and thermal cycling. The mismatch in thermal expansion coefficient is a primary stress inducer during thermal fatigue. The mismatch can be adjusted, however, by varying the filler content. Consequently, to develop an optimum design, a basic study was conducted to determine the relationship among particle size and size distribution, packing density, and thermal expansion coefficient. Based on this study a particular system was selected for bonding of a highly filled composite to glass.

The other areas addressed in this study was the use of coupling agents to promote adhesion. A variety of coupling agents and application methods were examined to optimize the bonding in this system. An important conclusion of the work is that both the filler type and the coupling agent play significant roles in retaining bonding during thermal cycling in a moist environment.

Environmental Attack

In most composite applications there is a need for resistance to attack by the various environments that can be present. Since polymer composites and polymer fibers are now being used in seals, gaskets, and similar applications, there are cases where this environment can be very severe. In several applied projects conducted during the past year, such was the case. As a result, tests were conducted to examine the resistance of various polymers to oxidation in hot acid or base. A data base was established indicating the resistance to degradation and in some cases information regarding the degradation mechanisms and products for a variety of materials. These materials included polyesters, polyamides, polyethers (such as cured epoxies), saturated hydrocarbons, fluorinated hydrocarbons, and polythioethers.

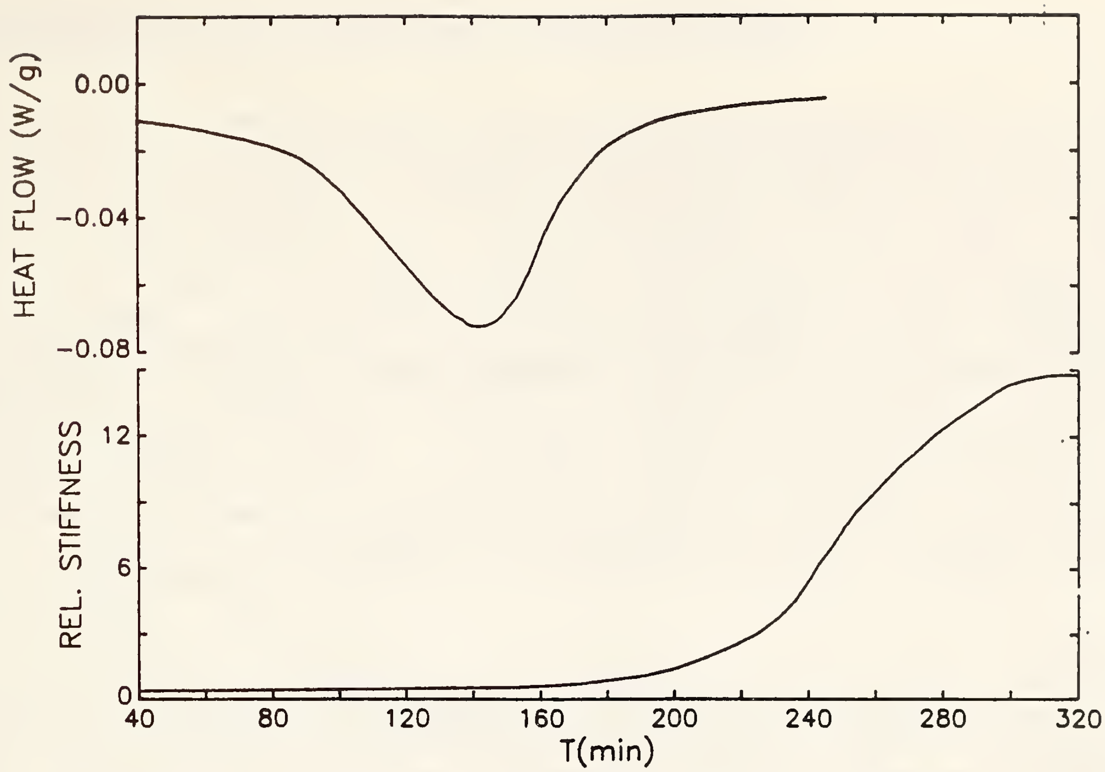

Figure 1. Isothermal Cure Monitoring of Epoxy Resin by Relative Stiffness and DSC at 60°C

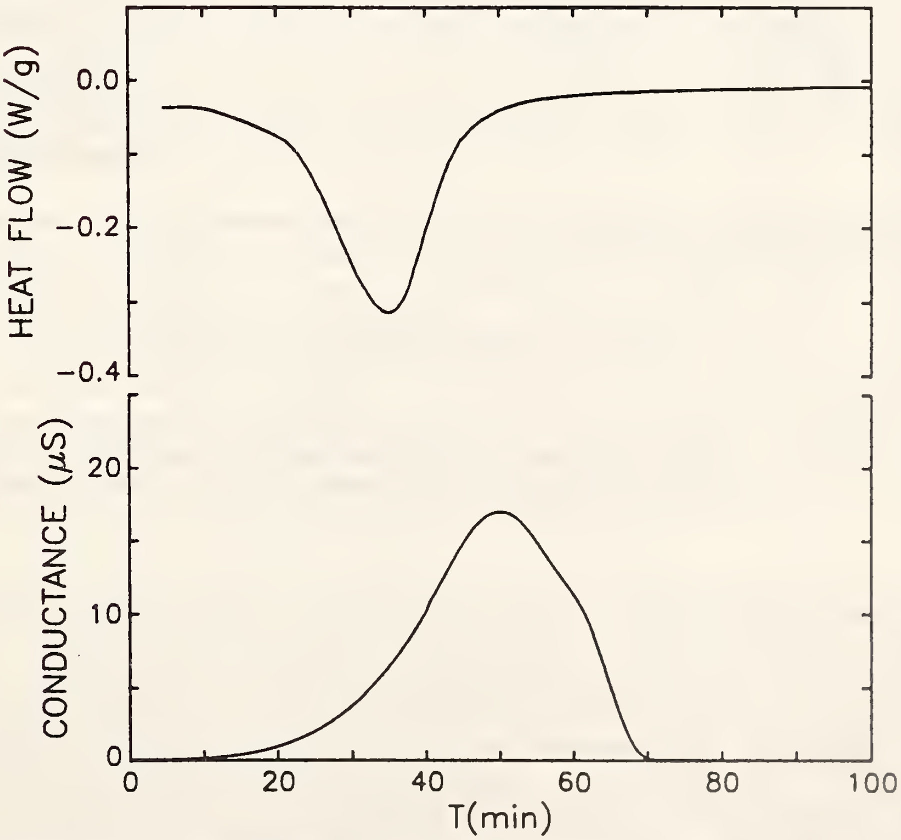

Figure 2. Isothermal Cure Monitoring of Epoxy Resin by Conductance and DSC at 80°C

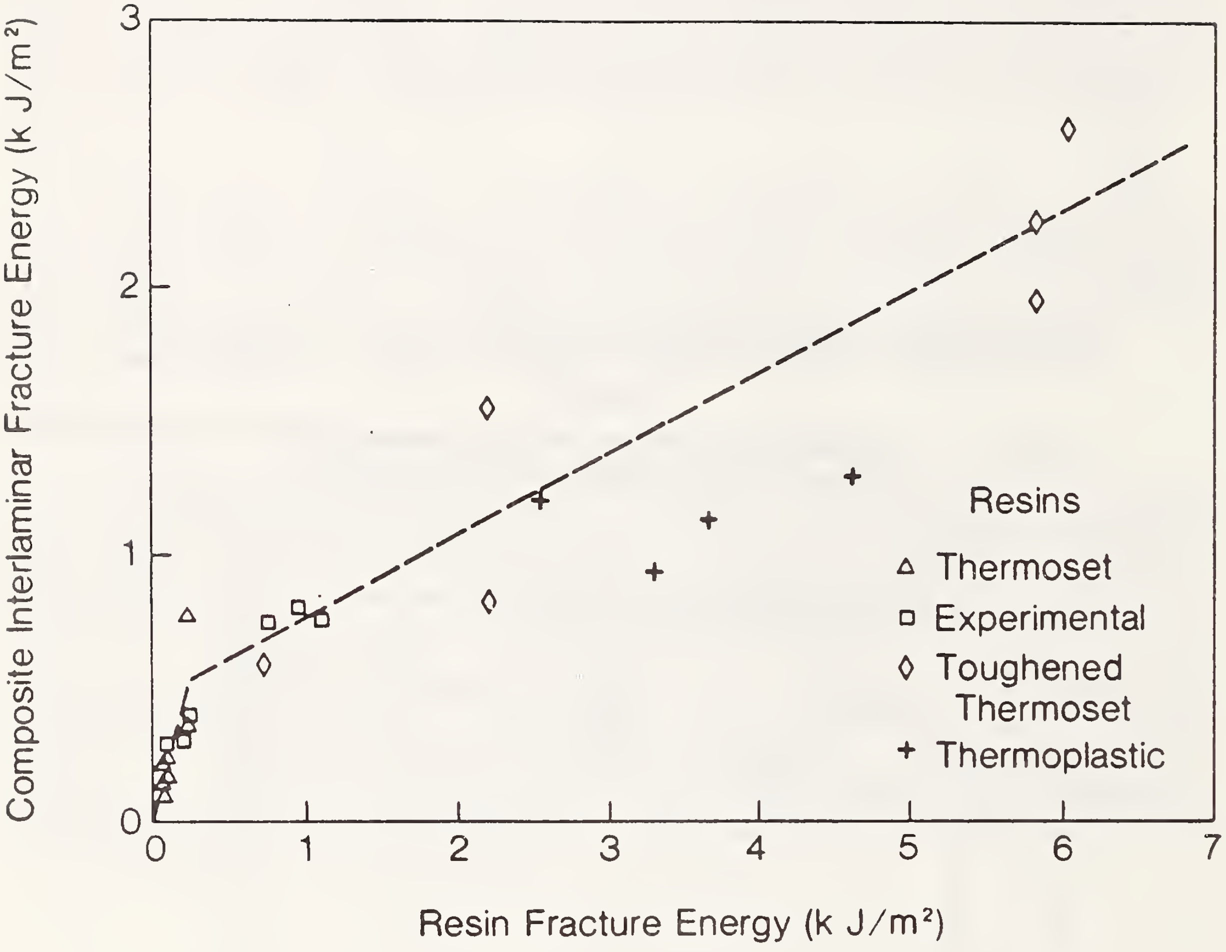

Figure 3. Relationship Between Resin and Composite Fracture Energies for a Wide Variety of Systems. Dashed Lines Indicate the General Trends in the Data.

MICROSTRUCTURE AND PERFORMANCE OF DIELECTRIC PLASTICS

Task 14339

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 by interested to our laboratories.

The measurement of the 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 ininduced 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.

FY 85 Significant Accomplishments

- Pressure gauges using poly(vinylidene), (PVDF) fluoride have been designed, fabricated and used successfully in other agency projects. Pressure transducers developed for imbedding in solid media for the measurement of shock-wave propagation were successful in tests performed at the Naval Surface Weapons Center. In work supported by the Bureau of Engraving and Printing, a second series of tests using PVDF pressure gauges on the Intaglio printing press at the Bank of England provided new data on pressure distribution with multiple layers of rigging.

- An automated, real-time AC conductivity measurement system has been used to monitor the curing of epoxy resins during early stages of cure. The value of conductivity and its evolution with time at a constant temperature shows promise of being a method of estimating the remaining shelf-life in a pre-mixed resin. Dipolar loss as measured with the dielectric spectrometer does not seem to be a useful technique on the system studied so far.

- The thermal pulse measurement of polarization distribution in polymer thin films has been tried using a variety of laser light sources. Based on the results, procurement specifications have been written for a light source thought to be suitable for examining the distribution of trapped charges near the surface of insulating polymers.

Automated Dielectric Measurements and Models for Dielectric Relaxation

Subtask 1 of Task 14339

F. I. Mopsik and K. J. Wahlstrand

During the past few years we have developed a time-domain dielectric spectrometer which records the transient charge response to an applied step voltage for times from 10 μs to 3000 s. The response is then numerically transformed into an equivalent frequency range of 10^{-4} to 10^{4} Hz. A commercial version of the instrument is being developed by IMASS Inc., Hingham, MA, through the Research Associate program at NBS. The speed of the measurement now allows us to examine the dielectric spectrum of materials which change as a function of time. To facilitate such measurements, a real-time clock has been incorporated in the instrumentation.

The dielectric spectrometer has been used to monitor the curing of epoxy resins but has been useful only in the later stages of cure when the initially high conductivity has been reduced by gelation. An automated real-time A-C conductivity measurement system was set up to monitor the early stages of cure. Such measurements have shown that AC conductivity at 50 Hz can monitor the cure. For the systems studied to date, conductance is the main feature that can be followed and there does not seem to be a major dipolar contribution to the loss that would be useful. There still remains the possibility that dipolar loss would be important in other systems but this is a point that needs clarification.

Conductance measurements have also been made on an epoxy that was partially cured prior to measurement. The results, when compared to resin that was not previously cured, show that once curing temperature is reached, the curing process resumes, for the partially cured resin, with a curve identical to the last part of that for the initially uncured resin. This suggests that a conductance measurement could be used to monitor the initial state of the resin, both to estimate shelf-life and to estimate the curing time needed for that batch of resin. A program is now being set up to establish the validity of this finding.

In a recent theory we proposed a soliton model of dielectric relaxation for the crystalline α-peak in polyethylene, accounting reasonably well for the observed dielectric data at constant temperature. However, experiments by Sayre et al. [1] show that the shape of the Cole-Cole plot depends on temperature. In particular, it is found that the Cole-Cole width parameter β increases with increasing temperature. We are exploring the temperature dependence of the soliton model in an attempt to explain this behavior and more generally characterize the model.

An analytical extension of the continuum limit theory to include temperature-dependent conformational defect populations was carried out. The defects were modelled as fixed infinite reflecting barriers to soliton motion. The resulting dielectric decay function was found to be not significantly different from the previously obtained Williams-Watts result. In addition, the function scaled with temperature, predicting a temperature-independent Cole-Cole plot, in contrast to the polyethylene experiments.

We are currently performing more stochastic dynamics simulations of the soliton model at varying coupling constants and temperatures to explore the temperature behavior in the continuum (large coupling) and noncontinuum limits. It has been found that the continuum limit autocorrelation function scales with temperature, with only a weakly temperature-dependent friction coefficient. However, simulation using "one-soliton" autocorrelation function data in the noncontinuum limit shows a power law behavior which changes strongly with temperature. The power increases with the ratio of coupling constant to temperature from negative values up to the continuum limit result of 0.5. This is believed to be a multiple soliton effect. It is hoped to relate this behavior to an analytical model as well as use it to explain the Sayre et al. experimental results.

[1] J. A. Sayre, S. R. Swanson and R. H. Boyd, J. Polym. Sci., Polym. Phys. Ed. 16: 1739 (1978).

Piezoelectric Polymers and Pressure Transducers

Subtask 2 of Task 14339

J. D. Barnes, A. J. Bur, M. G. Broadhurst, S. C. Roth, and
K. J. Wahlstrand

Poly(vinylidene fluoride), (PVDF), can be made piezoelectric by the temporary application of high electric fields. During the past several years NBS has played an important role in explaining the origin of piezoelectricity and pyroelectricity in this and other polymers. This fundamental understanding of the properties of the polymer is now being used in the development of pressure transducers for the U. S. Air Force, the Defense Nuclear Agency, and the Bureau of Engraving and Printing. In addition, we are examining the changes which occur at the molecular level as the polymer loses its activity when subjected to successively higher temperatures above 80 °C.

PVDF transducers offer the advantages of being tough, thin, flexible films with a broad-band frequency response and an acoustic impedance close to that of water (and therefore close to that of wet soil and human tissue). We are currently constructing pressure transducers to be characterized under conditions of high dynamic pressures (shock waves), varying thermal environment and dynamic shear stress.

Pressure gages, which will be used in soil and concrete environments, consist of two 12 μm thick films of PVDF which are laminated together using epoxy. The films are made piezoelectrically active over a region 1 cm in diameter by poling this area with an electric field of 2 MV/cm at room temperature. In order to use the gage in soil containing sharp particles, the PVDF is laminated between two 125 μm thick layers of protective material such as polycarbonate. We are investigating the response of such gages to shear stress and to shock generated pressure pulses. Gage output from an applied shear stress is of interest because in the field use of the gage we wish the piezoelectric shear coefficient to be as small as possible, i.e. a gage which responds to compression stress only is the most desirable. According to the model, the piezoelectric shear coefficient is zero, but, in practice, we measure a shear-stress response which is 10-20% of the response to an equivalent compression stress. Some modification of the model is needed. We hypothesize that the shear response is caused by a tilting of the polar crystallites in the shear field.

In collaboration with the Naval Surface Weapons Center, we are carrying out shock-wave experiments using the PVDF transducer as a detector. For these experiments, the bilaminate PVDF gage without protective layers was positioned between two 1.27 cm thick plates of PMMA using epoxy as an adhesive. The PMMA-PVDF assembly formed the target of a light gas gun. The shock wave was faithfully reproduced by the charge vs. time profile of the gage, an initial rapid rise due to the shock front followed by a plateau with a duration of 3-4 μs and then release to zero. The tests demonstrated the reliability of the gage at high pressures and short time. A calibration, carried out over the pressure range 0.4 to 1.6 GPa, showed that the response deviated from a linear extrapolation of low pressure (4-10 MPa) measurements. The nonlinear behavior is an expected observation resulting from the decrease in compressibility of PVDF as pressure increases.

Printing as an art has been with us for centuries. Printing as an empirical science is new. The United States Bureau of Engraving and Printing, as a participatory member of the Intaglio Research Group, is attempting to define some of the parameters of that science. Central to this attempt is the ability to make dynamic measurements of the pressure in the nip, or contact region between the two cylinders, of an intaglio printing press. The thinness, flexibility, and toughness of PVDF transducers provides a means of obtaining these data. During the past year, development experience gained in previous years was used to construct gages, calibrate them at low-frequency loading, and use them on a sheet fed intaglio press (similar to the type used to print all U.S. currency). On the rotating press, repetitive pressure measurements with pulse heights as high as 40,000 psi (2.8 x 10^8 Pa) and pulse widths on the order of 10 ms were successfully recorded. Placement of gages at different interfaces within the multiple layers of rigging material verified the validity of the assumption that the multiple layers act as a single homogeneous medium.

An increasing fraction of the piezoelectric activity of PVDF is lost as temperature is increased between 75 °C and its melting point of 175 °C. We have investigated changes in dipole orientation within the crystalline phase of the polymer by following changes in X-ray pole figures which accompany this thermal aging. The specimen of PVDF which we chose for these measurements was taken from a 50% crystalline, 1mm thick sheet. Processing of this sample, which was done at Thomson CSF, France, involved simultaneous mechanical rolling and electrical poling. Rolling is done in order to orient the c-axis of the crystals in the direction of roll (which also orients the ab plane of the crystals) so that the dipoles, which are normal to the c-axis, are placed in an orientation to receive the maximum torque from an applied field. X-ray pole figure observations of the as-received material revealed that the dipoles occupy sites which are ±30° with respect to the direction normal to the electrode.

Thermal aging consisted of cycling the temperature of the specimens between room temperature and successively higher maximum temperatures, T_{MAX}, with each cycle. At the end of each cycle, room temperature measurements of piezo- and pyroelectric activity, density and X-ray pole figures were made. Pyroelectric and piezoelectric coefficients decrease linearly with increasing temperature between 75 °C and 164 °C. Values of these coefficients at room temperature after heating to 164 °C were only 35% of their initial values (nearly independent of time at the elevated temperature). Extrapolation of these data predicts complete loss of activity at 207 °C, in close agreement with other predictions of a Curie temperature for PVDF.

The crystalline phase of our specimens was the pseudo-hexagonal β phase for which the positions of the dipoles in the ab plane have a near hexagonal configuration. A proposed six site model for dipolar orientation in the crystalline field is supported by our direct observation of the six sites in the spatial distribution of X-ray intensity from the (200) and (110) diffraction planes. Changes in diffracted X-ray intensity from these six sites as a function of thermal aging were interpreted as the rotation of dipoles by 60° steps away from the direction of primary polarization. Using this model of thermal depolarization, we calculated the fraction of dipoles which contributed to the piezoelectric activity as a function of the state of depolarization. The loss of polarization is attributed to a Curie transformation which extends over a very broad temperature range.

We have also continued our effort to understand these piezoelectric polymers from a theoretical standpoint. We view crystalline polymer molecules as having a rotational persistence length, several monomers long, and treat these segments as individual dipole units of moment, m. In the classical site model for dielectric relaxation in polymers, these dipoles move independently in a crystal potential having 2 or more minima separated by barriers. The model becomes quite interesting when (1) the dipole moment-electric field interaction energy, mE, is comparable to both the thermal energy, kT, and the crystal interaction energies, and (2) some cooperativity is included in the model. The rich and varied electrical behavior of ferroelectric polymers makes it possible to collect a large variety of both equilibrium and kinetic data with which to evaluate the parameters that make up such a cooperative site model.

In the past year we sought a mathematical description that mimics, as simply as possible, the hysteresis effects observed in ferroelectric polymers. We focused our attention on the predicted spacial averages, $\langle\cos\theta\rangle$ and $\langle\cos^2\theta\rangle$, where θ is the angle between a dipole moment and the applied field, (E), for comparison with quasi-equilibrium displacement charge, (D) vs. E and dielectric constant or infrared intensity vs E data for polyvinylidene fluoride. Generally we found quite good agreement between experimental data for PVDF and the behavior of the variable site model.

Space Charge and Ion Transport in Polymers
Subtask 3 of Task 14339

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[1] Foreign guest scientist from Ube Industries, Japan (Returned February 1985).

Polymers which can dissolve salts and conduct ions are an interesting and important class of materials. Since they can be inert to lithium and can be fabricated in thin films they have potential applications as electrolytes in high energy density batteries. Although the number of polymers which exhibit these properties is gradually increasing, most of them are based upon a high proportion of ether groups or amine groups in the polymer backbone or on side chains. Ionic transport occurs primarily within amorphous regions of semicrystalline polymers and the temperature dependence of ionic conductivity can be qualitatively described by the WLF relation which is based upon free volume concepts. A general phenomenon is that the dissolution of salts involves strong interactions between polymer molecules and the ions. Even monovalent cations act like cross-links which cause a large increase in the glass transition temperature and a corresponding decrease in mobility with increasing salt concentration.

During the past year, we have continued to investigate the properties of linear polyethylene imine $(-CH_2CH_2NH-)_n$, (PEI), to which alkali metal salts have been added. Crystallinity in this semicrystalline polymer is destroyed upon dissolution of the salts but in the case of NaI a new high melting crystalline phase involving the salt and the polymer is formed. As with all other polymers which have been studied so far, the DC conductivity passes through a maximum with increasing salt concentration. We have succeeded in improving the mechanical properties of the polymer and prevented crystallization of both PEI and PEI-NaI complex while retaining the ability to dissolve salts by light cross-linking with 1,2,7,8 diepoxyoctane. At 140 °C, the conductivity is comparable to that of polyethylene oxide (PEO) - salt systems but the conductivity of the cross-linked PEI decreases with decreasing temperature much more than the PEO system.

We have attempted to reduce the strong interaction between polymer chains induced by the presence of ions by quaternizing the nitrogen in the backbone of the polyethylene imine with butylbromide and ethylbromide. The quaternized polymers seem to be able to dissolve NaI but the T_g of the starting material is around 50 °C and DC conductivity is disappointingly low.

Most of our effort in the coming year will be directed towards obtaining a more basic understanding of the state of the ions in the solid polymer. In collaboration with personnel from the Center for Analytical Chemistry, we have made preliminary measurements using neutron-depth profiling which indicate that we should be able to measure the diffusion coefficient of $^6Li^+$ in polymeric electrolytes under a variety of conditions. From measured DC conductivity and ionic diffusion coefficients, we hope to deduce information about the fraction of the added ions that contribute to conductivity. Mobility of ions will also be compared with the mobility of uncharged species (e.g. cyclohexane) in the same systems to yield information about the general validity of models for ion transport in polymeric electrolytes.

Electromagnetically(EM) induced diathermy and hyperthermia for cancer treatment, and growth and healing of bones and tissue are of increasing importance. Dielectric tissue phantoms (dielectric materials that will behave electrically much like living biological tissue are used to evaluate equipment intended for the EM generation of heat in animal tissue. Presently-used phantoms are based on aqueous biopolymer gels which exhibit undesirable long-term changes of their mechanical and electrical properties. The Food and Drug Administration is seeking alternative non-aqueous non-biopolymer-based phantoms with improved stability. We are helping to design a synthetic-polymer based phantom as a measurement and calibration standard. This past year we have carefully measured and interpreted the dielectric data for biological tissue over 12 decades of frequency in order to fully understand the mechanisms whereby these materials are heated by EM fields. The heating is due to the conduction of ions dissolved in the aqueous tissue fluid and is modified by the partial blocking of the ion flow by the cell walls. Based on this knowledge we have designed a class of synthetic materials using propylene carbonate and ethylene carbonate as the liquid phase, one of several possible salts to supply mobile ions, and one of several possible gel forming polymeric materials to provide the interfaces to partially block ionic conduction and provide the concommitant increase in dielectric constant. We are currently obtaining systematic data on several potential phantom systems to establish the range of electrical and other physical properties that are obtainable with these synthetic phantoms and to confirm our understanding of the behavior of ionic conductors in general.

The Electric Power Research Institute is funding research at NBS directed toward improved polymeric electrically insulating materials for use as dielectrics in high voltage cables. The specific task of NBS is to gain an understanding of charging phenomena in nominally insulating polymers under high fields and moderately elevated temperatures. The gradual accumulation of charge and the kinetics controlling its distribution as a function of time are hypothesized to create potentially undesirable conditions in the insulation such as redistribution of the internal fields accompanied by local concentrations of the field strength, which conditions can result in poor ageing characteristics and ultimately in premature breakdown. An understanding of the charging behavior is expected to facilitate the development of modified polymers not prone to charging. The experimental phase of the work involves the measurement of charge-depth profiles in polyethylene and related materials using the thermal pulse method. In order to make measurements in the anticipated situations where the volume densities of space charge are small and sometimes concentrated near the sample surfaces, the experiment was redesigned to employ a high power, pulsed laser as the thermal pulse generator.

Preliminary laser thermal pulse experiments were performed using a variety of laser types (solid state, CO_2, dye) available outside the Polymers Division (Optical Physics, Fire Research) and outside NBS (U. of Maryland, Nav. Res. Lab.) with the aim of evaulating their suitability prior to procuring one for the project. On the basis of these measurements, it was concluded that a nonstandard laser was needed to generate pulses in the 100 ns to 10 µs range. One problem with standard Q-switched lasers is that the pulses generated are too short (10 ns) so that at useful energies per pulse, the peak powers are so high that the electrodes are vaporized in a single shot. Several design approaches were discussed with laser vendors, including designs which were previously used in other experiments with similar requirements. However, the procurement process, which was begun in late February 1985, failed to turn up concrete bids from vendors reluctant to provide NBS with a custom pulsed laser heating system until the Fourth Quarter when a freeze in previously committed funds has delayed the procurement until the next fiscal year.

The preliminary experiments showed that polyethylene films previously subjected to an applied electric field of 0.1 MV/cm at ca. 100 °C for 1 hour gave thermal pulse-induced electrical response signals. These signals indicated that charge carriers were present in the bulk. The signal strength, mean duration and shape were observed to depend on charging field, temperature and time and furthermore to evolve with the passage of time after charging. By contrast, samples subjected to electric fields at room temperature showed negligible charging when the measurements were made, usually one day after charging.

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Industrial and Academic Interactions

Industrial

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

The natural gas utilities, materials suppliers, and Gas Research Institute are cooperating with the Polymers Division to produce reference polyethylene materials of the sort used in gas distribution systems. The reference resin, pipes, and joints will be distributed to laboratories conducting research and tests on polyethylene parts used in gas distribution, and will provide for more meaniful intercomparisons of results from different laboratories.

The American dental industries continued to display strong interest in and support for the dental materials program. The research associate agreement with Dentsply International was extended for one year, and another dental manufacturer explored use of NBS user facilities and a research associate arrangement. Several dental manufacturers supplied special alloys for casting studies, and others provided specimens of new composites for NBS scientific research. A glass developed at NBS has been incorporated into a commercial composite formulation, and NBS developed vanillated cements have been used as the basis for a new line of products.

Plans were made for cooperative work with IBM San Jose Laboratories on vibrational spectroscopy of polyethylene and on scanning tunneling microscopy of polymer molecules.

Industrial/Academic

A cooperative program has been initiated to investigate the effects of processing on the network structure of epoxy resins. Texaco and Prof. R. Stein of the University of Massachusetts are participating in this effort. Texaco is providing the raw materials and using calorimetry to monitor the cure reactions that occur during processing and NBS is determining the cure kinetics by IR measurements and characterizing the network structure from neutron scattering experiments. A postdoctoral fellow at the University of Massachusetts is working part time at NBS to assist in data collection and analysis. The objective of the project is to understand how processing influences the network structure in thermosetting resins.

In cooperation with the Polymer Science and Engineering Department at the University of Massachusetts and the Research Department of the Celanese Corporation, NBS is participating in research on polymer blends under the sponsorship of the Defense Advanced Research Projects Agency. The primary goal of this academic/industrial/government research effort is to develop new polymer alloys which can be used in engineering applications at high temperatures (300-450°C). The effort at NBS is focussed on relating the thermodynamics and kinetics of phase separating blend systems to physical properties.

Joint research among scientists at the University of Pittsburgh, Exxon, and NBS is aimed at characterizing the viscoelastic behavior of cyclic macromolecules in the melt. Exxon scientists are providing the samples, and researchers at NBS and the University are conducting the mechanical properties measurements. The focus of the work is to compare the viscoelastic properties of cyclic macromolecules with those of the linear analogs as a test of reptation theories of macromolecules dynamics.

Academic

C. M. Guttman carries out theoretical studies of chain conformation in the semicrystalline state of polystyrene, in collaboration with Prof. J. D. Hoffman, University of Maryland and Dr. Z. Kifle, who is now at the University of Cincinnati but was a Research Associate of the Polymers Division until February 1985.

F. W. Wang carries out measurements of diffusion in polymeric systems by a photobleaching method in collaboration with Prof. E.-S. Wu, University of Maryland, Baltimore County.

The failure behavior of toughened polymers is being studied in cooperation with Dr. S. S. Wang at the University of Illinois and Dr. A. J. Kinloch at Imperial College. NBS is determining the fracture behavior; the University of Illinois is conducting finite element analysis studies and Imperial College is characterizing the morphology, all on the same multiphase polymer systems. The ultimate objective is the development of structure - property relationships for such materials.

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

A joint program to obtain an analytic solution for the correlation function associated with neutron scattering by molecular networks such as epoxies is underway with Prof. H. Benoit of CRM Strasbourgh, France. Success in this effort would directly benefit other projects using neutron scattering to characterize network structure.

Five guest workers from domestic (2) and foreign (3) universities are associated with the Dental Materials Group. A cooperative seminar series was established with the University of Maryland Dental School. Several finite element modeling studies on dental material-tooth systems are in progress with the University of Illinois, Chicago. One guest worker from Georgetown University is a key investigator on bonding of dental resins to dentin. Guest workers (residents) from the Naval Dental School work with several investigators within the group.

Associated Activities

Invited Talks

Division personnel presented a total of 141 invited talks on research activities at the following types of organizations and symposia: industrial laboratories, 17; international symposia, 17; universities, 45; topical symposia, 26; national and government laboratories, 16; professional society meetings, 11 and Gordon Conferences, 9.

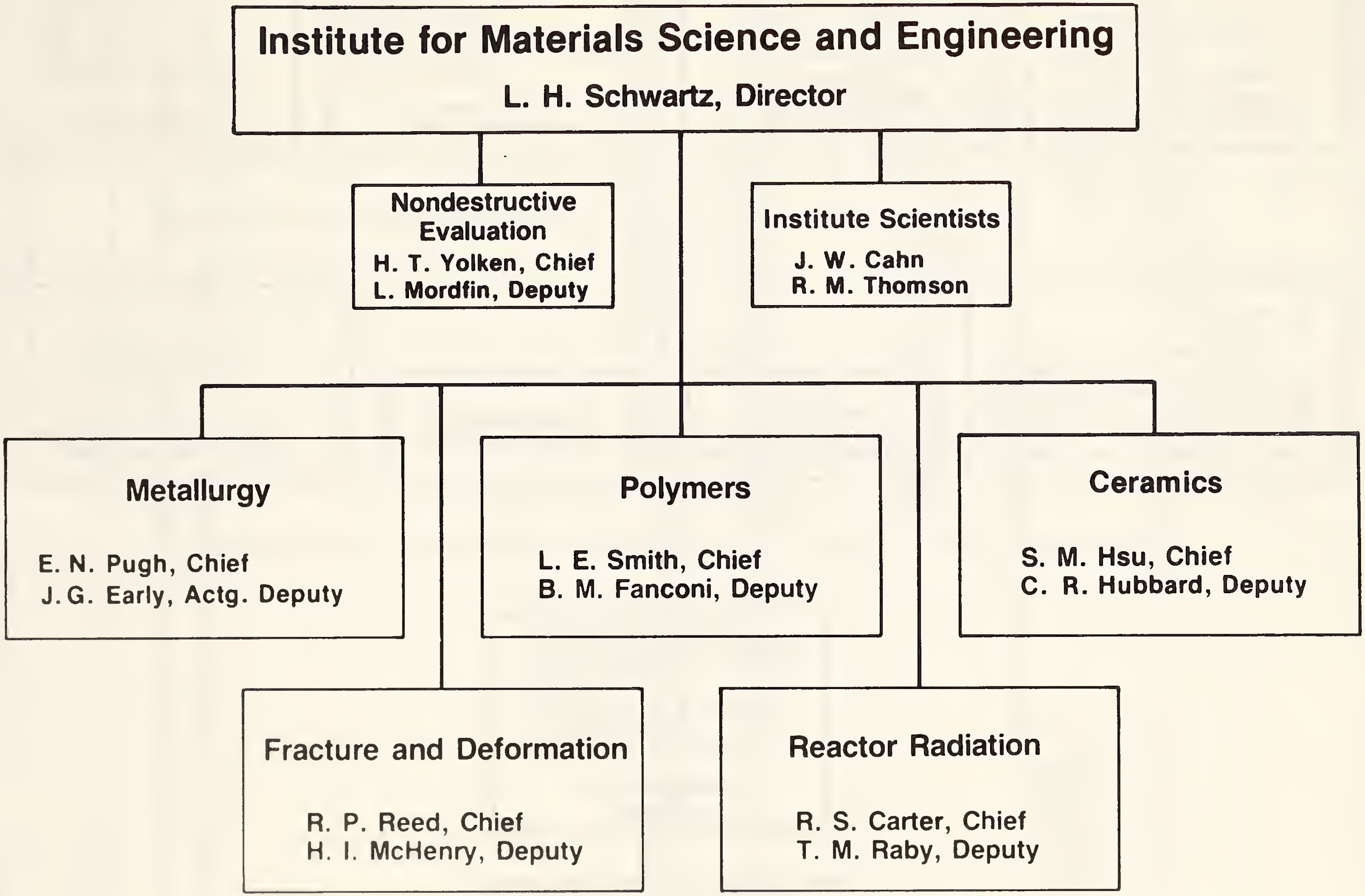
Conferences Sponsored

The Society of Plastics Engineers (SPE) and the National Bureau of Standards jointly hosted a symposium on October 15-17, 1984 to discuss industrial applications of polymer phase diagrams. Phase diagrams are graphic displays that contain data and information about the physical and chemical states of materials and the thermodynamic transformations between these various states, or phases. The purpose of this Symposium was to focus the attention of the polymer scientific community on the utility of polymer phase diagrams in solving technical problems. The keynote speaker at the Symposium was Professor Paul Flory, 1974 recipient of the Nobel Prize in chemistry for his contributions to polymer science. The Symposium concluded with a workshop discussion, led by a panel of industrial, government, and academic scientists, that identified the types of phase diagram information most needed in industrial applications and suggested directions for future research in polymer phase equilibria.

SRM's

Three rubber and rubber compounding standard reference materials have been certified for physical properties. These materials are used by the rubber industry for process control and to conduct standard ASTM tests.

The certificate for a poly(methyl methacrylate) SRM is being drafted. This SRM will be used by the polymers industry to calibrate instruments used to measure the molecular weight and molecular weight distributions of acrylic type polymers.



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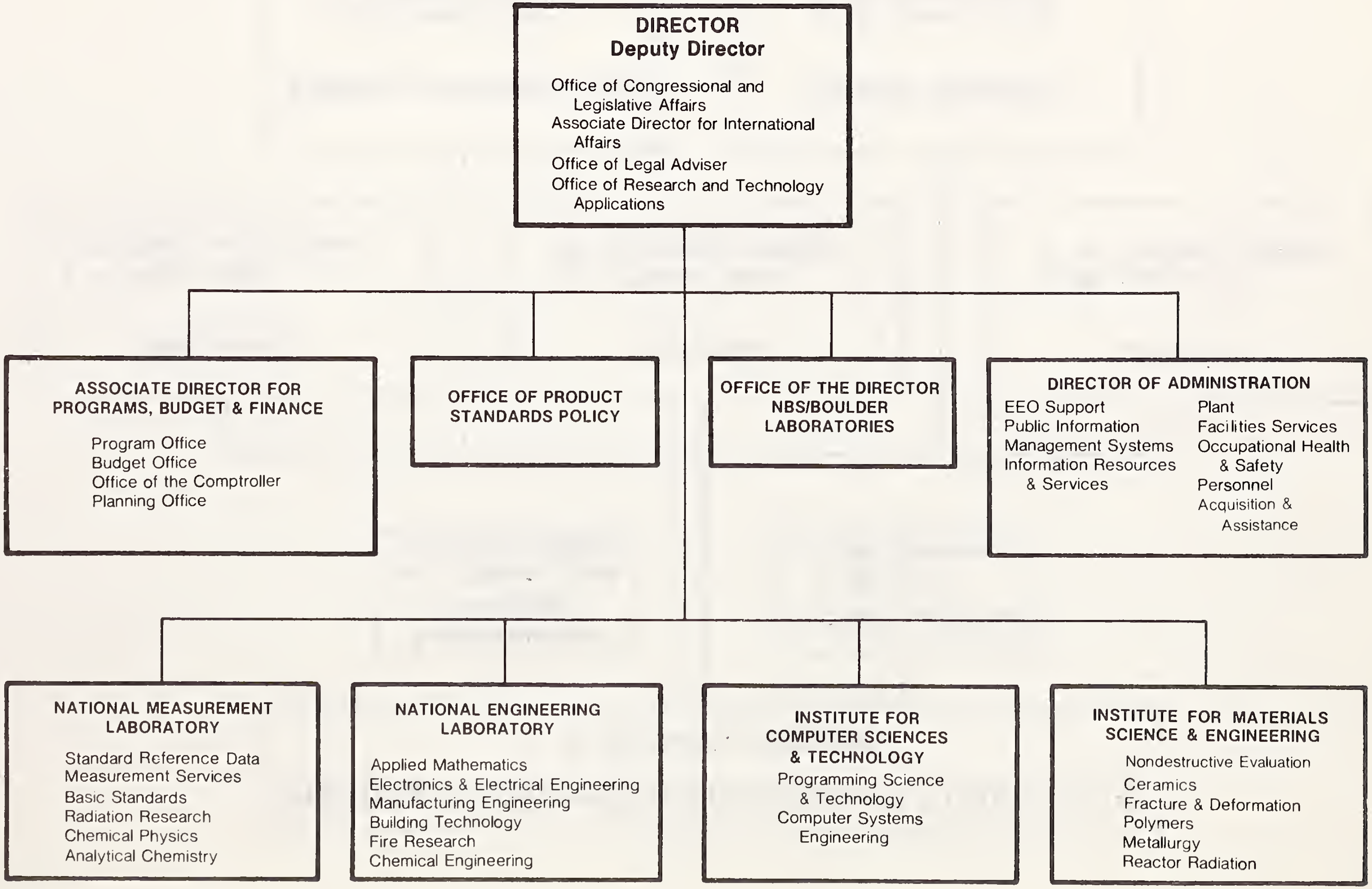

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Polymers Division, Gaithersburg, MD 20899

10. SUPPLEMENTARY NOTES

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

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

Technical Activities of the Polymers Division for FY 85 are reviewed. Included are descriptions of the 6 Tasks of the Division, project reports, publications, and other technical activities

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

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

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