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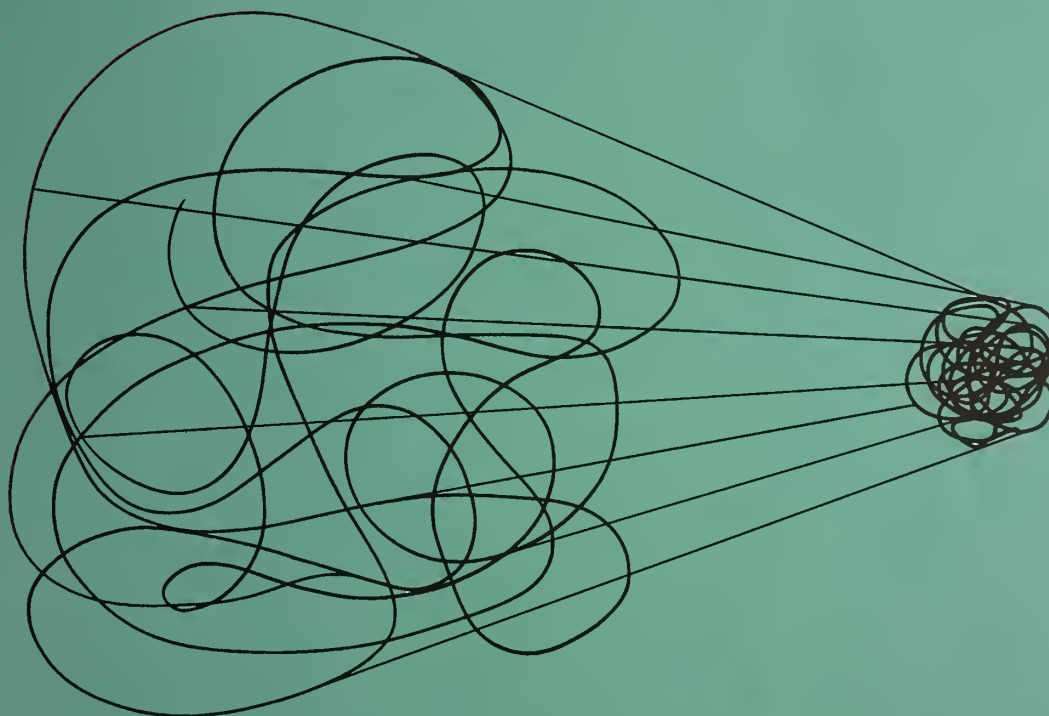
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**NBSIR 81-2263**

Center for Materials Science

# Polymer Science and Standards Division



**Annual Report 1980**

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The cover drawing is a schematic representation of the collapse transition in polymers. It converts a random coil structure of low density to one of high density. This change can be brought about by small changes in either temperature or solvent composition and has been suggested as a biological amplifier. A theoretical description of this process has been developed by Sanchez. See page 21.

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POLYMER SCIENCE AND STANDARDS DIVISION

Annual Report 1980

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(301) 921-3734



## Polymer Science and Standards Division



**RONALD K. EBY, Chief.** Dr. Eby was born in Reading, Pennsylvania in 1929. He earned the Sc.B. in physics at Lafayette College and the Sc.M. and Ph.D. at Brown University. Before joining NBS in 1963, he conducted polymers research in the Plastics Department of E. I. du Pont de Nemours & Co., Inc.



**LESLIE E. SMITH, Deputy Chief.** Dr. Smith was born in New York in 1941. 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.



**ANTON PETERLIN, Assistant Chief.** Dr. Peterlin was born in Yugoslavia in 1908. He earned the M.S. in mathematics at the University of Ljubljana and Ph.D. in physics at the University of Berlin. From 1939 to 1960 he was professor of physics in Ljubljana and from 1949 to 1959 was head of the Josef Stefan Institute. Before joining NBS in 1973, he was director of the Camille Dreyfus Laboratory.



**MARTIN G. BROADHURST, Group Leader, Electrical Properties.** Dr. Broadhurst was born in Washington, D.C. in 1932, and earned degrees in physics at Western Maryland College and Pennsylvania State University. After teaching at Penn State, he joined NBS in 1960.



**BRUNO M. FANCONI, Group Leader, Structure and Properties.** Dr. Fanconi was born in Merced, California in 1939. 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.



**JAMES M. CASSEL, Group Leader, Dental and Medical Materials.** Dr. Cassel of New Kensington, Pennsylvania was born in 1918 and earned the Ph.D. in chemistry at Georgetown University. He joined NBS in 1946 and today guides a program of research for improved dental and medical restorative materials.



**ISAAC C. SANCHEZ, Group Leader, Characterization and Standards.** Dr. Sanchez was born in San Antonio, Texas in 1941. He earned degrees in physical chemistry at St. Marys University (Texas) and at the University of Delaware. Prior to joining the NBS staff in 1977, he worked at the Xerox Research Laboratories and was on the Polymer Science and Engineering faculty at the University of Massachusetts.

**LESLIE E. SMITH, Acting Group Leader, Chemical Durability.**





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POLYMER SCIENCE AND STANDARDS DIVISION

Ronald K. Eby, Chief  
Leslie E. Smith, Deputy Chief  
S. M. Thomas, Administrative Assistant  
B. M. Weeks, Secretary

In the seven decades since Leo H. Baekeland introduced the first commercial synthetic plastic produced entirely by the reaction of small molecules, polymers have left little of our culture and technology untouched. We have moved rapidly into an age in which an overwhelming number of humanity's needs are served by polymers. The increase in production and use has been spectacular; the volume of polymers produced last year exceeded that of steel. Recent summaries show that polymers research already accounts for about forty-seven percent of the total industrial R&D expenditure for metals, polymers, and inorganic materials. Among these materials, polymers also constitute about thirty-nine percent of the value added by manufacture (a measure of the relative economic importance of manufacturing among industries), forty-five percent of the number of scientific publications, and thirty-nine percent of the ASTM standards.

Polymers have been shaped by intellectually sophisticated research which has been recognized by a number of Nobel Prizes. The resulting materials have contributed to national productivity through their economy, ease of fabrication, and useful properties such as low density, corrosion resistance, and toughness. They are energy efficient, with the largest volume polymer, polyethylene, using twenty-eight percent of the energy per unit volume required by steel for the conversion from raw to refined material and yielding further savings in processing and shipping.

Polymers have entered increasingly sophisticated and demanding applications. Polyvinylidene fluoride films are used as electromagnetic transducers in high fidelity systems. Structural parts of aircraft are composites with a polymer matrix. Polyurethane elastomers are used to pump blood in circulatory assist devices. The list of such examples is very long, encompassing trends for the increased use of polymers in packaging, construction, transportation, energy, electronics, information handling, clothing, appliances, dentistry, and medicine. Since polymer technology is on the steep part of the learning curve, these trends create new needs for concepts, measurements, standards, and data that can be used to insure reliable performance in use, processing, and other phases of the material cycle.

To identify the key needs, the managers of the Polymer Science and Standards Division make structured visits to government and industrial laboratories. Recent visits have included Bell Labs, Du Pont, Army R&D Command, General Motors, Boeing, and Lawrence Livermore. Surveys have been conducted in the areas of durability, processing, and composites. These and other contacts with experts in industry, trade associations, standards associations, government, and academia insure that the Division's efforts are directed toward fostering the effective use of polymers in solving national problems cited by our Director as appropriate for NBS. These include the growth of industrial productivity, prudent utilization of energy sources, a reasonable system for regulation of the effects of technology, and a wise policy of materials utilization.

The Division has used its survey activities as a basis for participating in budget initiatives to secure the resources necessary to meet the emerging needs. For the budget cycles currently active, programmatic initiatives that include additive migration, composites (biaxial orientation), blends, ionic conduction, and thin films are under consideration. Competence building initiatives on the science of collapse transitions, electronic conduction, high field NMR, and electron microscopy have been prepared.

The present activities are associated into areas concerned with mechanical reliability in load bearing applications, chemical durability, and lifetime prediction including the migration of protective additives, characterization methods and standards for molecular composition and use properties, dielectric properties, and electrical conduction, and reliable dental and medical materials. Substantial cooperative efforts are conducted with the Food and Drug Administration, the Department of Defense, the National Institutes of Health, the American Dental Association, the Department of Energy, the Bureau of Engraving and Printing, and others. All the efforts lead the scientists in the Division into productive examination of those

properties of polymers which are of concern to people who use, design, and produce useful polymer objects. This work helps society capture, in safe and satisfying ways, the benefits of the increasingly widespread application of polymers.

In the following pages, the activities of the Division are presented formally in five Tasks, each described separately:

DIELECTRIC AND PIEZOELECTRIC PLASTICS PERFORMANCE

POLYMER STANDARDS FOR CONTROL AND EQUITY

MIGRATION AND THE DURABILITY OF POLYMERS

MECHANICAL DURABILITY OF POLYMERS FOR DESIGN AND USE

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



## DIELECTRIC PLASTICS DESIGN AND PERFORMANCE

M. G. Broadhurst

Task Leader

Trends in dielectric application of polymers include use of higher working voltages in electrical apparatus and transmission lines to conserve materials, save space, and reduce weight. This work provides manufacturers (polymer manufacturers, film fabricators, transducer manufacturers), trade associations (EPRI), and government agencies (DOE, DOD) with data, measurement methods, and concepts which identify limitations in polymer performance traceable to manufacturing practices. For example, steam curing of extruded polyethylene insulated cables results in lifetime limiting voids and inclusions. With a trend toward increased use of underground transmission of electric power, improved insulation performance is required. Data and recommendations from this work go directly to cable manufacturers and funding organizations (i.e., EPRI, DOE) who are able to specify and require manufacturing changes leading to improved products.

Other trends are new, rapidly growing applications of polarized polymers as pyro- and piezoelectric transducers. Transducer manufacturers as well as private and government transducer users (DOD, EPA, HHS) need reliable information connecting polymer structure and polymer performance to the design of improved transducers. This work will help transducer material and device manufacturers design and develop commercial polymer transducers for use in health and safety applications (pulse monitors, therapeutic and diagnostic sound measurements, auto crash sensors, prosthetic fitting devices, nontoxic antifouling coatings, mine disaster warning devices) and in the areas of national security (microphones, hydrophones, intrusion detectors, ultrasonic and infrared imaging devices, fuzing devices, etc). Important scientific opportunities of this work include breakthroughs in understanding the basic factors in electrical failure of polymers and discovery of novel measurement methods which are becoming possible with newly developed polymers. For example, this work attempts to show how polymers interact with electronic and ionic charges and how structure can be modified to optimize piezoelectric and semi-conducting properties.

### Polymer Insulation for Superconducting AC Power Transmission Cables

F. A. Khoury, F. I. Mopsik, S. J. Kryder, and L. H. Bolz

This project, sponsored by and carried out in collaboration with Brookhaven National Laboratory (BNL) with DOE funds, is part of a program for evaluating the suitability of various types of polymer films for use (in tape form) as the electrical insulation in high power superconducting AC transmission cables operated at 6-8 K. Such cables, in which the superconductor is  $Nb_3Sn$ , are currently under development at BNL. Among the guidelines used for selecting the insulation for such cables is that the dielectric constant ( $\epsilon$ ) should be 2.5 or less and that the dielectric loss ( $\tan \delta$ ) should preferably not exceed  $20 \times 10^{-6}$  at the cable operating temperature range and 60 Hz.

This subtask is primarily concerned with the measurement of the dielectric properties ( $\epsilon$ ,  $\tan \delta$ ) of polymer films at cryogenic temperatures. These measurements, for which NBS has a unique instrumental facility, are coupled with studies of aspects of the fine structure of the films in an effort to determine the influence of various structural parameters (e.g., crystallinity, molecular orientation, voids) on the dielectric properties of the films. In addition to determining whether specific types of commercially available films meet the established criteria for dielectric properties, these studies are aimed at providing data relevant to the design and production of films exhibiting optimum dielectric properties for the intended end use. In a less extensive effort, the compressibility of the polymer films is measured. This latter feature is relevant to the determination of the optimum conditions (e.g., tape tension) necessary for winding the films (sliced into tapes) around the cable core, so as to yield a cable exhibiting appropriate flexibility for winding onto storage drums 10 feet in diameter.

In FY80, this project was mainly concerned with studying laminates made from two layers of a new,  $\sim 50 \mu m$  thick polypropylene bound together by a polyurethane layer. Measurements made last year indicated that these laminates had substantially lower loss than ones made from older, thinner ( $25 \mu m$ ) polypropylenes and could meet the requirement that  $\tan \delta$  not exceed  $20 \times 10^{-6}$  at 6-8 K, which the older ones could not.

Dielectric loss studies were made on two series of laminates. The two series had different yellow dye concentrations (0.7 percent and one percent) in order to see if the presence of dye affected the dielectric loss. The dye is added for visual monitoring of tapes made from the laminates as they are wound to form the cable insulation. In both cases,  $\tan \delta$  was  $12-15 \times 10^{-6}$  at 6-8 K, indicating that the added dye did not affect the loss and that the loss criterion could be met.

Another series of measurements was made on laminates of nominal 80, 100, and 120  $\mu\text{m}$  thickness from polypropylenes of 40 and 60  $\mu\text{m}$  thickness. In addition, the 60  $\mu\text{m}$  polypropylene film was measured separately. These graded thicknesses for the laminates will be used in a cable made for voltage testing to better distribute the voltage stresses across the insulation. The results showed that the loss at 6-8 K decreased with increasing thickness showing that the polyurethane layer, which had a constant thickness in all the laminates, contributed significantly to the loss. The values for  $\tan \delta$  were  $18-20 \times 10^{-6}$  for the 80  $\mu\text{m}$  laminate and  $10-12 \times 10^{-6}$  for the 120  $\mu\text{m}$  laminate. The loss for the polypropylene alone was  $6-7 \times 10^{-6}$ , one of the lowest values seen for any polypropylene. These data were then combined to show that the suitably low loss of the present laminate as compared to the older, less satisfactory, laminates was due both to the intrinsically lower loss of the polypropylene itself and to the reduction in the amount of polyurethane present, since only one bonding layer was needed.

In other dielectric measurements, an epoxy composite that was intended for use in bushings was measured for dielectric loss.

All the laminates measured dielectrically were also measured for compressibility when stacked in layers. These data are necessary for predicting cable bendability. The series of graded laminates was also examined microscopically. There was a considerable reduction in void content in the polyurethane layer compared to earlier laminates. This indicates better control over the laminating process and a reduction in possible breakdown problems under voltage stress.

Successful improvement of these materials is traceable in large part to the measurements and analysis from this work which is fed back to the manufacturers to guide processing changes.

#### Polymer Tape Insulation for Oil Impregnated AC Power Transmission Cables

F. A. Khoury, F. I. Mopsik, S. J. Kryder, and L. H. Bolz

Oil impregnated paper (cellulose) tape has been, for many years, one of the most commonly used types of electric insulation in high power AC transmission cables. The current and projected needs for more efficient power transmission systems have elicited considerable interest in the development of oil impregnated or oil filled cables operated at 700-1000 KV, in which polymer tape insulation will be used instead of the conventional paper tape which is unsuitable because of its large dielectric loss.

In a project sponsored by Brookhaven National Laboratory with DOE funds, a program has been initiated in the Polymer Science and Standards Division for evaluating the suitability of various types of impregnated AC transmission cables. The goals of this study are: (a) the measurement of the dielectric constant and dielectric loss of candidate films between 273 K and 423 K; (b) the determination of the dependence of the dielectric loss on the fine structural characteristics of the films; and (c) the specification of the dielectrically most suitable type of film for the intended end use.

The dielectric measurements carried out this past year have focused on a series of drawn polyethylene tapes prepared for Brookhaven by Battelle Institute. Three different base polymers were used under two different rolling conditions. The conditions were a roll temperature of 298-303 K with a thickness reduction ratio of 5-7, and a roll temperature of 348 K with a thickness reduction ratio of 8.3. All the samples were measured under standard temperature cycling to check the effects of thermal cycling.

The three different polyethylenes showed quite different loss characteristics. One of them exhibited a low level of loss ( $\tan \delta$  less than  $30 \times 10^{-6}$ ) that did not change much on thermal cycling. The other two had an initial  $\tan \delta$  at 303 K of  $80 \times 10^{-6}$  and  $50 \times 10^{-6}$  all at 100 Hz. The latter two showed substantial reductions in loss at 303 K with thermal cycling to



353 K, 373 K, and 383 K in three successive sets of measurements. All the specimens showed substantial changes in dimensions as reflected in the measured capacitance. The reason for these loss differences as well as the changes in loss with thermal cycling is unknown. One possibility may be differences in the raw polymer (cleanliness and additive content). There were some hints that relatively volatile materials did contribute to the loss. No correlation was found with sample density.

The density, wide angle x-ray diffraction, and small angle x-ray diffraction of the samples were measured both before and after thermal cycling. The most notable effects were found in the density. The tapes rolled at 298-303 K had an increase in density corresponding to an increase in crystallinity from ~66 percent to ~75 percent, while those rolled at 348 K had an increase of crystallinity of ~72 percent to ~77 percent. Some samples of one of the tapes rolled at 298-303 K were thermally cycled as in the dielectric measurements and forwarded to Brookhaven for measurement of thermal conductivity changes induced by the thermal cycling. These data are important for predicting the dissipation of heat generated during power transmission.

The results summarized above, coupled with earlier measurements on the effect of thermal cycling on the dielectric properties of the experimental polyethylene tapes made by Battelle Institute, have emphasized the need for modifying processing conditions in order to produce tapes which are dimensionally and dielectrically stable to thermal treatments in the range 273-383 K. It is expected that the normal operating temperature of the cables will be 355-365 K.

### Structure and Performance of Piezoelectric Polymers

G. T. Davis and M. G. Broadhurst

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

While piezoelectric and pyroelectric activity from polymers is comparable to that from good ceramic materials, other properties of polymers often make them the preferred transducer material. Some of the polymer properties which make them so useful include toughness, flexibility, low density, broad band response, close acoustic impedance match to water, and ease of fabrication. The interest in the use of polymeric transducers continues to increase as evidenced by the requests from other government agencies, by the large number of requests for information by mail, phone, and personal visits, and by the 20 papers presented at the American Physical Society meeting in March 1980.

During the past year, considerable effort was expended in the preparation and characterization of gamma phase PVDF in order to investigate its poling characteristics. A surfactant, siloxane-oxalkylene block copolymer (L-520) produced by Union Carbide was deposited from ethanol solution onto PVDF powder so as to comprise two weight percent additive. The alpha phase which forms upon cooling from the melt is transformed to gamma phase when heated in the presence of the surfactant at 1°/min to 176 °C. Films without the additive, subjected to the same thermal treatment, melt and recrystallize in the alpha form when cooled. X-ray diffraction is the most convenient means of distinguishing between the two crystal phases. (IR and DSC are less definitive). Films of alpha and gamma phases were subjected to the same poling conditions, and the piezoelectric and pyroelectric responses were measured. The much larger response from gamma phase for all electric fields less than 1.25 MV/cm confirms that this is a polar crystal phase. The value of 1.3 nC/cm<sup>2</sup>K for pyroelectric coefficient after poling for 10<sup>3</sup> seconds at 80° and 1 MV/cm is almost the same as that reported for unoriented beta phase obtained by pressure quenching and poled at the same field for one hour at 23 °C. For values of electric field 750 kV/cm and greater, the alpha phase undergoes the electric field induced phase transition to a polar form, so that at 1.25 MV/cm the responses from alpha and gamma phase films are comparable. It has not been possible to pole at fields greater than 1.25 MV/cm because of electrical breakdown. In the course of this investigation we discovered that simply orienting the polymer film reduces electrical conductivity by more than a factor of 100. An improvement in electrical breakdown strength is indicated but not fully quantified at this time. Because of the field-induced phase transition of alpha phase, there seems to be no practical advantage for promoting the formation of gamma phase unless one must be confined to low poling fields. A detailed report on these results is in preparation.

We have also poled PVDF as it undergoes the alpha to gamma phase transition in the vicinity of 176 °C for the purpose of studying the stability of the resultant piezoelectric film. Unfortunately, the breakdown strength at these temperatures is about 400 kV/cm so that only low activity is achieved, and the response resulting from these low poling fields decays with time even at room temperature.

We have recently succeeded in increasing the piezoelectric and pyroelectric charge response (as opposed to voltage response) of PVDF by improving the coupling between the polar crystals and the external electrodes. A 0.1 M solution of tetrabutyl ammonium bromide in dichloroethane was diffused into a poled film which greatly increases the conductivity of the film. The initial pyroelectric activity of 2.4 nC/cm<sup>2</sup>K increased to 3.3 nC/cm<sup>2</sup>K. (Solvent without the electrolyte has no effect.) As the volatile solvent is removed, the response returns to its initial value but can be increased again by the sorption of dichloroethane from the vapor phase. A more highly poled sample subjected to similar treatment increased from an initial value of 3.3 nC/cm<sup>2</sup>K to a maximum value of 4.4 nC/cm<sup>2</sup>K. When the exposure time to the electrolyte solution was increased from 1 day to 3 days at 23 °C, the activity as we measure it was greatly reduced, presumably because the impedance of the polymer film becomes comparable to or less than that of the measuring circuit. Preliminary experiments using the same salt in the much less volatile 1,6-dichlorohexane have shown similar enhancements without loss of the enhanced activity with subsequent storage time at ambient conditions. These investigations are continuing.

In the past year we published a summary of a cooperative six-site model for ferroelectric switching in  $\beta$ -phase PVDF. This model predicts the essential features of polarization and IR transmission hysteresis curves and data on crystal plane reorientation with applied field. These data all apply to changes that occur well below the order-disorder (or Curie) transition implicit in the model and occurring in PVDF well above the melting point. This past year, Dr. Furukawa published data on a copolymer of PVDF and trifluoroethylene which showed a Curie temperature at 70 °C. It was possible then to extend the model calculations to the transition region. The experimental observation that the critical switching field decreased with increasing temperature and vanishes at 70 °C is consistent with the model, as is the anomalously high dielectric constant which has a maximum of about 70 at 70 °C. Using structural information, this dielectric constant anomaly was calculated for the six-site model. As expected, the calculated dielectric constant for the crystal phase was considerably larger than that for the semicrystalline sample. This occurs in any composite since the lower dielectric constant component reduces the electric field in the higher dielectric constant component. Because the particle shapes and orientations are so important in composite dielectrics, we are not able to calculate exactly what the semicrystalline sample dielectric constant is, even if we know the dielectric constants of the components. However, it looks as if there are some significant trends in the data not predicted by the model. A complete publication of the calculations to date is in preparation.

#### Automated Dielectric Measurement

F. I. Mopsik, S. J. Kryder, and S. C. Roth

The automated dielectric spectrometer is nearing completion. This instrument will record the transient response of a dielectric sample in real time and using numerical transforms will automatically determine the dielectric constant and loss of the sample over the frequency range of 10 kHz to 0.001 Hz or below. The instrument should have a resolution of 10<sup>-5</sup>, which is an order of magnitude improvement over most designs. This will allow determination of the dielectric properties of low loss polymers with much greater speed than previously possible.

Work done in FY80 includes completion of the charge detector. This detector can resolve 0.1 pC with a 10  $\mu$ s rise time and for time up to 100 s. A major challenge that was overcome was the design of a reset circuit so that the output could be zeroed with negligible charge transfer or drift. In addition, the final interface boards have been acquired. Currently, the computer interconnections are being made prior to testing as a complete unit.

In addition, some of the programming for data treatment has been tested by its use with the thermal pulse experiment. In particular, the idea of data selection and interpolation for optimal computation has been successfully incorporated in the thermal pulse experiment and will be used in the spectrometer. This allows the actual data sampling to be done in an experimentally convenient manner with a sufficient excess of points to obtain significant noise reduction.



## ASTM Activities

W. P. Harris

Mr. Harris chaired the final meeting of his six year chairmanship of ASTM Committee D-9, Electrical Insulating Materials, at Dearborn in October 1979. There he received an award of appreciation for his excellent service. He attended the March 1980 ASTM meeting in Dallas and continues to serve as a member of the executive committee. Current activity in D-9 consists of revising D-150, which is one of the committee's most widely used and cited testing documents.

### Polymer Sensors for NDE

S. Edelman and S. C. Roth

The 1980 NDE work of the Electrical Properties Group consisted of the use of polymer sensors to measure dynamic elastic moduli and to detect wear in airplane control cables.

Making use of the sensitivity, low density, and flexibility of piezoelectric polymer strain gauges, we have worked out a non-resonant method for measuring both the real and imaginary parts of both the dynamic Young's modulus and the dynamic shear modulus of structural materials in the form of long, thin rods. All four quantities can be obtained as continuous functions of both frequency and static load. The frequency can be varied over a wide range, and the static load can be varied from a large compressive value through zero to a large tensile value.

The method can be used to study the basic dynamic properties of materials. It should be especially useful in studying composite materials and polymers, materials whose dynamic properties are likely to vary with static load. In the case of composite materials, variation of damping characteristics with static load can be expected to be a sensitive test of the quality of the bonding between components. The method can be used to provide basic engineering data needed for designing structures which are to be subjected to dynamic stresses or for which particular levels of internal damping must be obtained.

Since all measurements are made on a single specimen under identical conditions (except for the type of excitation) any deductions about the internal structure are free of the uncertainties introduced where measurements at different frequencies require different specimens and where measurements of the different moduli require different apparatus. The method can be used for nondestructive evaluation of structural elements either for compliance with design specifications or for monitoring a change in properties during service. A paper describing the method was presented at the April 1980 meeting of the Acoustical Society of America. Support for a laboratory installation to apply the method is being sought.

The study of airplane control cables is being performed on an apparatus in which the cable, under tension, is pulled around a small pulley by a cam which converts the rotation of an electric motor to reciprocating motion. A polymer sensor, attached to the cable near the pulley, detects the noise of the motion of the strands as they deform on the pulley. The sensor can be removed from the cable and reattached readily so that the same sensor can be used to compare different cables or different conditions. An elaborate mechanical filter eliminates motor noise from the signal. A spectrum analyzer operates on the sensor signal, and changes in the spectrum are monitored to detect the effects of fatigue and wear.

### Polymer Stress Gauge for Intaglio Printing Press

M. G. Broadhurst, S. C. Roth, S. J. Kryder, A. S. DeReggi, and S. Edelman

This work, which is supported by the Bureau of Engraving and Printing, U.S. Department of Treasury, involves the development of a gauge to measure the dynamic pressure at critical points in the presses used to print money. The first phase of the work was completed last year. The accomplishments of the first phase included measurement of the width of the area of contact between the two cylinders of the press, the duration of contact of a point on the upper cylinder with the lower cylinder, and a qualitative (uncalibrated) determination of the change of the pressure with time during contact.

This year work began on the second phase which is to provide calibrated pressure measurements. Specifications for telemetry have been written and equipment ordered. Dedicated data processing equipment has also been ordered. Preliminary design and construction of polymer gauges is well along. A start has been made on design of a field calibrator for checking the calibration of pressure gauges after installation.

### Ultrasonic Hydrophone

A. S. DeReggi, S. C. Roth, J. M. Kenney, and S. Edelman

This project is partly sponsored by the Bureau of Radiological Health, which is contributing the services of a guest worker. One objective of the project is to develop a piezoelectric polymer hydrophone for characterizing, point-by-point, the acoustic field beamed by ultrasonic transducers, such as those used in biomedical equipment. Accurate knowledge of the details of the acoustic field is not otherwise obtainable. The knowledge can be used to ensure both the safety and adequacy of ultrasonic dosage and for research in ultrasonic treatment.

During this year, the performance of several prototype hydrophone probes has been investigated thoroughly, with regard to both frequency response and performance stability at room temperature. The sensitivity, the broadband responsivity, the non-perturbing properties, and the long-term stability have been judged good enough for the Bureau of Radiological Health to adopt the probe as a standard probing hydrophone. A paper is currently under review for publication in the Journal of the Acoustical Society of America. In addition, a patent is being sought.

Several prototype annular arrays have been constructed and tested. These arrays consist of concentric ring-detectors formed as common parts of a tensioned polymer membrane. They are being used in ultrasonic research to verify ideas in the theoretical modeling of disc-shaped ultrasonic projectors. The geometry of the polymeric arrays allows the measurement with unprecedented precision of the relative contribution of the ring diffraction term and the piston plane wave term of the projected acoustic beam. This work is the subject of the Ph.D. dissertation of our guest worker, Gerald Harris of the Bureau of Radiological Health, who is also a part-time student at Catholic University. A preliminary account of this work has been submitted for presentation at the 25th Annual Meeting of the Institute of Ultrasound in Medicine in New Orleans on September 15-19, 1980 and for publication in the Proceedings of that Conference.

### Durability of Piezoelectric and Pyroelectric Activity in PVDF

J. M. Kenney and M. G. Broadhurst

This work was initiated with the Naval Undersea Systems Command because of their interest in widespread use of polymer hydrophones by the U.S. Navy. Since good durability of activity is crucial for this application and since long time testing makes it difficult to judge the effects of structural or processing modifications on durability, we have developed a short time test procedure which will give a rapid measure of relative durabilities of different samples. The test consists of continuously recording pyroelectric activity while the temperature is being increased linearly to the melting point of the sample. Samples show a broad maximum in activity vs. temperature. We use the temperature at which the activity falls as a measure of durability--the higher the temperature the more durable the sample.

Dramatic differences were seen between samples of PVDF and a copolymer of PVDF with tetrafluoroethylene. The temperature at which the activity falls to zero is 100 °C for the copolymer and 170 °C for the PVDF.

While this short time test will be useful for comparing effects of different structures and treatments, it must be calibrated with longer time aging studies. This year we made measurements of 38 PVDF samples which had been stored at room temperature for 15 months. It was found that the activity of the specimens as a fraction of the initial activity was  $0.91 \pm 0.05$ . The magnitude is similar to that measured at two DOD laboratories in previous studies.

The mechanism of loss of activity of PVDF has not yet been established, and these measurements should provide valuable data for the development of a suitable aging model.



## Space Charge Studies

A. S. DeReggi, F. I. Mopsik, and M. G. Broadhurst

The static and kinetic effects of space charge in polymers subjected to electric fields continues to be of interest as different groups in the USA and outside are developing new methods to measure these effects. In the poling of piezo- and pyroelectric polymers where near-breakdown fields are applied temporarily and in the standing-off of high potentials by polymeric electrical insulation where moderate fields are sustained for extended periods of time, space charge is either initially present as an ionic impurity, is produced through field-enhanced degradation, or is injected across the electrode-polymer interface. The space charge typically distorts the applied electric field and gives rise to regions of field concentration. In the case of insulation, there is a resultant acceleration of the aging process leading to premature breakdown. In the case of piezoelectric polymers, there is a resultant non-uniform distribution of polarization which in combination with a small but finite conductivity gives rise to unusual transduction phenomena.

Until recently, only qualitative information was obtained about the space charge and polarization distributions because of the preliminary stage of development of the methods used to measure these distributions. For example, using the thermal pulse method we were able to show that in PVF subjected to a poling voltage, polarization tends to reside near the negative poling electrode for a wide range of poling voltages and poling times and furthermore, that a threshold mean field of  $\sim 150$  v/ $\mu$ m must be exceeded in order for significant remnant polarization to be found. Extremely weak remnant polarization was measured for mean fields as low as 24 v/ $\mu$ m. We suppose that positive space charge plays an important role in producing a distribution of electric fields in the sample and hence a distribution of applied poling fields. These observations are markedly different from those made on PVDF where polarization tends to reside near the positive poling electrode (presumably due to negative space charge) and where there is a more gradual increase in remnant polarization as a function of the mean applied field. A paper discussing the role of space charge on the poling behavior of PVF has been written with a recent guest worker, Professor Sidney Lang of the Ben Gurion University (Israel), and has been submitted for publication in *Ferroelectrics*.

We have recently been able to acquire the transient charge response from the thermal pulse experiment in digital form, and the computer programming for data analysis has been completed and tested. From the data, one extracts the coefficients of a Fourier series representing the polarization distribution in the film. When data can be obtained by illuminating first one side of the film and then the other, the sum and difference of the two signals yield only even or only odd Fourier coefficients. This separation of terms facilitates a good determination of the thermal time constant  $\tau$  for the sample. An important feature of the program is that data are not chosen at equal increments of time but are taken at times chosen to yield the most information about the relaxation time of the  $n$ th term which varies as  $\tau/n^2$ . When data are available by pulsing alternate sides of the film, as many as ten Fourier coefficients can be determined. This means, very roughly, that the "resolution" is about one-tenth of the film thickness. This amount of detail in the charge and/or polarization distribution is expected to be of great value in directing the development of models for non-uniform field distribution during the early stages of poling.

## Piezoelectric Polymer Fuzing

S. C. Roth, A. S. DeReggi, and S. Edelman

This project is sponsored by the U.S. Army Armament Research and Development Command. It is developed from previous work by NBS in cooperation with Frankford Arsenal reported in NBSIR 75-724 (R). NBS is to assist ARRADCOM to determine the feasibility of using piezoelectric polymer film in impact sensors for fuzing applications in several particular geometries.

An equation was developed describing the performance of piezoelectric polymer in fuzing. When reasonable values, supported by the results of impact studies, were used in the equation, it was predicted that sufficient energy would be released to detonate a 105 mm high energy antitank round.

A technique using heat, vacuum, and pressure was developed for shaping piezoelectric polymer to the inside of an ogive (forward part of a munitions casing). An ogive instrumented in this way was delivered to ARRADCOM for testing.

A draft of the final report has been sent to ARRADCOM for comment and approved by them.

### Development of Piezoelectric Polymer Stress Gauges for Rock Studies

S. C. Roth and S. Edelman

This work, funded by the Denver Mining Research Center of the Bureau of Mines, is a continuation of work described in the report for last year to measure noise from grinding together of rock specimens.

Most of a series of polymer gauges for measuring rock noises were developed at NBS and delivered last fiscal year. The remaining gauges have been constructed and will be delivered this fiscal year. The gauges have been effective in detecting and measuring the acoustic emission from rock samples under stress. Also, they have been found to survive collapse and crushing of the rock specimens unless a crack develops directly across the active area. Future work on rock and soil transducers is expected to result from tests on these transducers.

#### Thick Electrode Transducers

A. J. Bur and M. G. Broadhurst

The fabrication of transducer specimens of  $PVF_2$  with thick, well adhering electrodes was attempted. The objective was to study the influence of the mechanical properties of the electrodes on the  $PVF_2$  transducer behavior. It is expected that the hydrostatic response will be enhanced by a factor of two to three if the electrodes maintain their own integrity and exert a stress on the polymer film during temperature and/or pressure changes. Transducers previously fabricated in our laboratory have had very thin evaporated electrodes, several hundred angstroms thickness. Because the electrode is so thin, the mechanical properties of the polymer substrate dominate.

Metals such as Ni, Au, Ag, and Cu have elastic moduli which are 30 to 40 times larger than that of  $PVF_2$ . A metal electrode of 0.4  $\mu m$  thickness will have the same rigidity as 12  $\mu m$  of  $PVF_2$ . A metal electrode of 4  $\mu m$  thickness will have 10 times the rigidity of the polymer. Relative to the polymer, a thick electrode can be considered rigid so that when the polymer contracts, a stress between electrode and polymer develops. The predicted effect of this stress is to enhance the change in the thickness of the polymer film by a factor of two or three relative to the change with thin electrodes.

Previous attempts to detect a significant electrode thickness effect have been unsuccessful, presumably due to poor adhesion between polymer and metal. This year we have made measurements on a series of specimens furnished by Bell Telephone Laboratories which showed a systematic dependence of piezoelectric response due to stretching in the plane of the film with different thicknesses of gold making up the electrodes. As in previous studies, we have yet to find a large difference (more than 10-20 percent) in pyroelectric response or hydrostatic piezoelectric response before and after the gold electrodes are removed. The differences we see in the activity of these specimens with electrode thickness seem to be due in part to differences in sample polarization.

We suspect that stiff electrodes inhibit polarization of these films by restricting the local strains needed to accommodate changes in crystal phase and orientation which occur as part of the poling process. We are presently conducting experiments to measure this polarization for specimens with differing electrode stiffness to characterize this effect. We are making sure that the polarization measurements made during poling agree with those made while the specimens are depoled (melted) and will then depole the Bell Lab specimens to determine their state of polarization.

As a final attempt to measure thick electrode effects, we have arranged to obtain samples from EMI with well attached electrodes of differing thickness. If these do not show the expected effects, we will be forced to conclude that the effect does not exist, though no explanation for its absence has yet been found.



## Fabrication of Piezoelectric Polymer Film

A. J. Bur and M. G. Broadhurst

The Department of the Navy is supporting a project to fabricate piezoelectrically active PVDF specimens with thicknesses of 0.79 mm (31 mil). A thick transducer is desired because it will have a lower capacitance than the thin film PVDF transducers which we have routinely prepared and a correspondingly higher voltage response for a given strain.

The problems with making thick polymer transducers are the large stresses needed to stretch thick samples and the large voltages needed to apply a polarizing field to them. Large Instron machines were used to stretch our materials while the high voltage group at NBS assisted in poling them. Initial failures at poling thick samples were due to low breakdown strength which we suspected was an inherent disadvantage of thicker, more defect prone samples. Further investigation, however, showed that there was a large difference between oriented and unoriented material. The oriented material is able to withstand poling fields of 1 MV/cm so that acceptable transducer activity can be achieved. We have not established the quantitative difference in breakdown strength between unoriented and oriented PVDF, but qualitatively it can be concluded from these observations that such a difference exists.

To better understand this dependence of breakdown strength on stretching, we measured the resistivity of stretched and unstretched PVDF from several sources. The data distinctly show that the resistivities for unoriented PVDF are lower than those for the oriented material by at least an order of magnitude. While we have not established a relationship between resistivity and breakdown strength, we conclude that the state of orientation is an important factor which affects the electrical properties of PVDF.

Molecular orientation is extremely important to making successful thick polymer hydrophones. These thick hydrophones are equal to, and may exceed, the performance of present state-of-the-art ceramic hydrophones. The use of this effect to study the basic nature of conduction is equally important scientifically.

### Diffraction From Nonperiodic Structures: The Molecular Conformation of Polytetrafluoroethylene (Phase II)

E. S. Clark<sup>1</sup>, J. J. Weeks, and R. K. Eby

The crystal structure of polytetrafluoroethylene has been a subject of discussion among spectroscopists, crystallographers, and others. However, the determination of structure in synthetic polymers is made difficult by the lack of resolution in the diffraction data. The diffuseness of the reflections observed in most x-ray fiber patterns results from the small size, misorientation, and imperfect lattice nature of the crystallites. This lack of resolution leads to poor accuracy in measurement of peak position and makes determination of layer line heights difficult with a corresponding loss of significant figures in evaluation of the repeat distance for the molecular conformation. In helical conformations, the repeat distance may be of considerable length or indeterminate and, in effect, nonperiodic. Remarkable electron diffraction patterns of the low temperature form of polytetrafluoroethylene have been obtained which exhibit layer lines sharply resolved to the 26th order. These patterns permit accurate measurements of the layer line heights. Equations have been developed to relate these heights to a molecular conformation defined in terms of an incommensurable helix of ratio,  $r = u/t$ , defining a conformation of  $u$  motifs regularly spaced along  $t$  turns of the helix. The electron diffraction data yield a molecular conformation of  $r = u/t = 2.159$ , with the molecule slightly untwisted from the previously assigned conformation of  $r = 13/6 = 2.167$ . The newly determined conformation corresponds within the limits of error to  $r = 948/439$ . However, the practice of expressing a helical conformation in terms of some commensurable ratio,  $u^*/t^*$ , is questionable. If the helical conformation is not expressed accurately in terms of simple small numbers, it is preferable to define the conformation in terms of the ratio,  $r$ , limited to the number of significant figures. This point is made tellingly in the present case where a change of one standard deviation in  $r$  changes  $u^*/t^*$  from 948/439 to 54/25. Furthermore, the error limits admit 82 other possibilities for  $t^* < 500$ .

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<sup>1</sup>University of Tennessee.

## Order-Disorder Transitions in Polytetrafluoroethylene

J. J. Weeks, I. C. Sanchez, C. I. Poser<sup>1</sup>, and R. K. Eby

The phase diagram of polytetrafluoroethylene has been enlarged by differential scanning calorimetry to include the concentration of hexafluoropropylene comonomer units. The two transitions near 292 and 303 K in the homopolymer move to lower temperatures with increasing concentration and apparently become one at a small concentration. Analysis of the data for this single transition yields 295 K for the temperature and 13.2 J/g for the heat of transition of an infinitely large homopolymer crystal. The heat of transition associated with the formation of a crystal defect is 0.021 eV. The qualitative features of the transitions can be accounted for by a mean-field model which involves two order parameters corresponding to planar units and helix reversals. This model yields two transitions which move closer together and to lower temperatures with increasing comonomer concentration. Decreasing lamellar thickness will have a qualitatively similar effect.

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<sup>1</sup>Guest worker, University of Massachusetts.

## POLYMER STANDARDS FOR CONTROL AND EQUITY

I. C. Sanchez

Task Leader

This task provides molecular and gas transmission standard reference materials (SRM's) to a 30 billion dollar/year plastics and elastomers industry. Molecular SRM's are used extensively in 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 processability and its ultimate performance.

Our basic mission is to maintain and extend our expertise in polymer physical characterization. A fundamental knowledge of polymer solution properties such as osmotic pressure, viscosity, diffusional behavior, and scattering power is essential to this goal. As a consequence, a majority of the activities in this task involve experimental and theoretical studies of polymer solution properties. Some of these activities during the past year include:

- o Production of a new, narrow-fraction polystyrene standard, SRM 1479 ( $M_w \sim 10^6$ ).
- o Completion of a new computerized gas permeation measuring facility.
- o Continued development of a new state-of-the-art, self-calibrating GPC; self-calibration is achieved by making simultaneous light scattering measurements at nine angles on the GPC effluent
- o Characterization, by intrinsic viscosity and light scattering measurements, of a ultrahigh molecular weight polyethylene used in prosthetic devices.
- o Development of the concept that all dilute polymer solutions possess certain "universal" physical properties characterizable by a single excluded volume parameter.

### Standards For Gas Transmission Rate Measurements

J. D. Barnes

Engineering work on the new NBS automated manometric permeation measuring facility is substantially complete. Operational trials and calibration measurements are currently under way. The efforts expended on the design of safety interlocks, control circuitry, interfaces, and operating software have provided valuable experience for future ventures in measurement automation. There are some improvements which must be made to the temperature controls and the vacuum manifold before routine experiments can be conducted.

Recent trends in gas transmission measurements have been toward instruments that are simpler to manipulate and more selective than the manometric technique. Our experience with our automated measuring system indicates that the manometric method is capable of considerable improvement at a relatively modest cost. The time scale of the measurements is determined completely by the diffusion coefficient of the gas, the thickness of the film being measured, and, in some instances, the time scale of concomitant viscoelastic processes. These factors are independent of the technique used to measure the transport properties. The optimization that is built into the controlling software we have devised does, however, result in significant time savings because there is no need for a human decision regarding the recovery of the system from the previous measurement cycle or the achievement of a steady state. The experience should prove useful to those who wish to devise simpler instruments for use in quality control applications.

The new facility was used to investigate the feasibility of adding transmission rates for He, N<sub>2</sub>, and CO<sub>2</sub> to the certificate for gas transmission SRM 1470, which is currently certified only for oxygen. These preliminary experiments demonstrated that the apparatus obtains valid data for these gases. An experimental design has been formulated for carrying out the measurements of transmission rates of He, N<sub>2</sub>, O<sub>2</sub>, and CO<sub>2</sub> at a number of pressures and temperatures as required for an SRM certificate. OSRM is providing support for these



measurements, and it is expected that they will be complete by the third quarter of FY81. The measurements of O<sub>2</sub> permeance are being redone because it is expected that some aging of the material has taken place during storage.

Correlations which are possible when four different gases with different molecular sizes and different thermodynamic properties are measured on the same sample should provide a clearer picture of the gas transport mechanisms in this polymer.

The preliminary experiments revealed, as expected, that CO<sub>2</sub> exhibits the phenomenon of partial immobilization in SRM 1470. New models must be devised for fitting the experimental data, and the ramifications of partial immobilization on the mechanical properties and morphology of the polymer must be explored before we can specify the best way to use SRM 1470 in calibrating CO<sub>2</sub> permeance measuring apparatus.

A publication describing the construction and operation of the automated manometric permeation measuring apparatus will be prepared as time becomes available once the apparatus is being used for routine measurements.

After completing the recertification of SRM 1470, we expect to evaluate candidate materials for an SRM with transmission rates approximately 50-100 times that of SRM 1470. These materials are needed because existing instrumental methods perform poorly at high gas fluxes. It is likely that minor changes will have to be made in our interfaces in order to accommodate the higher data collection rates found in this work.

Work is continuing on devising a system of units that is both compatible with SI and scientifically consistent. The SI base units of moles, meters, pascals, and seconds are the starting point. While the logic of this scheme is recognized, there is considerable resistance from users of the wide variety of customary unit systems.

A publication outlining ways in which SRM 1470 can be used to improve the performance of existing gas transport measurement systems is in preparation.

NBS played an influential role in promulgating a substantially revised edition of ASTM D-1434, the standard method for measuring gas transmission rates. The new document features more consistent terminology, an improved set of SI units, the use of safer equipment, the use of SRM 1470 for calibration checking, and a clearer derivation of the equations used to fit the data.

#### ASTM Activities

J. D. Barnes

J. D. Barnes serves as chairman of ASTM Subcommittees F-2.30 (Test Methods) and F-2.93 (Statistical Matters) of ASTM committee F-2 on Flexible Barrier Materials. Subcommittee F-2.30 is currently working on test methods relating to materials characterization, barrier properties, sealing and bonding properties, and additive migration. Subcommittee F-2.93 is responsible for providing statistical assistance to all task groups operating within F-2. The design and analysis of interlaboratory testing programs are the major forms this assistance takes.

Dr. Barnes and Dr. John Mandel conducted a workshop on Interlaboratory Testing during the February 1980 ASTM Committee Week in San Diego, California. Over 100 individuals from ASTM Committees D-20, F-2, and F-17 participated. Interlaboratory testing programs are the principal technique used to validate ASTM Methods of Test.

Dr. Barnes is also a member of ASTM Committee D-20 (Plastics) and its subcommittees on Plastic Film and Sheeting D-20.19, Olefin D-20, and F-2. Dr. Barnes led the task group that recently promulgated a revised version of ASTM D-1434, the standard Method of Test for Gas Transmission Properties of Plastic Film and Sheeting.

## Self-Calibrating Gel Permeation Chromatography

P. H. Verdier

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

We are designing and constructing a light-scattering detector for the GPC which measures, in real time, the scattering intensity as a function of scattering angle, and which is controlled by a dedicated minicomputer in a way that allows scattering to be measured as a function of scattering angle and concentration. The instrument will allow continuous monitoring of the variation of scattering with angle. This will allow immediate identification of difficulties such as association, microgel formation, etc., which could affect the validity of the molecular weight obtained, an important consideration for work on new and unstudied materials. In addition to molecular weight, the mean-square radius (radius of gyration) will 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 instrument has been designed, and construction of its mechanical components is scheduled for completion by the end of the current fiscal year. The dedicated minicomputer system has been installed, with a video display which will permit real-time plotting of the angular dependence of the scattering. In the coming fiscal year we expect to assemble and align the instrument and begin testing.

### Dynamics of Polymer Chains

P. H. Verdier and D. E. Kranbuehl

The dynamic behavior of polymer chains is important for two reasons. First, 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, non-equilibrium 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.

Second, the processability 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. Our 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 previously shown that for our simple chain models, self-entanglement effects lengthen the longest relaxation times of the chains by a factor proportional to about the first power of chain length. However, our models differ from polymer chains in solution in (at least) two obvious respects: the chains are constrained to lie upon a lattice, and motion from one configuration to another is accomplished solely by a series of purely local chain motions. Theoretical work carried out elsewhere appeared to predict a much weaker dependence of the lengthening of relaxation times upon chain length than we had found, leading to the suggestion that our results were artifacts arising from special constraints in the local chain motions we had employed. We subsequently obtained results for chains with modified rules of motion free of these constraints and showed that the suggestion was incorrect. We have now completed a series of studies of the effects of local bead motion constraints and of the type of lattice employed upon relaxation behavior. The results show that although self-entanglement effects are weakened by the removal of local bead motion constraints, they are still much stronger than current theoretical predictions. Further, the self-entanglement effects are essentially the same on simple cubic, body-centered cubic, and face-centered cubic lattices, suggesting that similar behavior may be obtained when the chains are removed from the lattice. Therefore, we are preparing to study the motion of chains free of lattice constraints (though still employing local bead motions). Testing of the programs is currently under way. We expect that it will be completed and preliminary results obtained by the end of the current fiscal year; the study should be completed in the coming fiscal year.

Additional work planned for the coming year will proceed along two lines. First, there is at present an unresolved disagreement in the literature regarding the interpretation of the time-correlation functions obtained for flexible chain molecules in the quasielastic light scattering experiment. It is not clear whether these functions exhibit the entire spectrum of chain relaxation times or are dominated by the longest relaxation time. It appears that by direct simulation we may be able to resolve the disagreement, which will increase the value of measurements made by this relatively new technique. Second, as a step in the direction of investigating melt properties, we will extend the simulation studies to non-dilute solutions.

### Static and Dynamic Scattering From Polymers

C. C. Han

Scattering techniques are most effective in measuring space as well as space-and-time correlations of polymers in both solutions and bulk states. Our effort has been centered around the universal approach of temperature, molecular weight, and concentration dependence of static and dynamic properties of polymers. We investigate and compare theoretical predictions based on modern scaling concepts as well as conventional theories to our experimental results from the small angle neutron scattering (SANS), light scattering, and quasielastic light scattering experiments.

In static scattering, spatial correlations of monomer densities in  $q$ -Fourier space are measured directly. With the SANS facility at NBS, it is possible to measure single chain properties in the range of  $0.01 < q < 0.1 \text{ \AA}^{-1}$  from dilute solution to the bulk state through deuterium labeling. Also, with the high concentration labeling technique which we developed last year, it is possible to study single chain properties over a wide range of concentrations using a medium flux reactor such as the NBS reactor.

On the other hand, dynamic scattering, such as quasielastic light scattering, uses the photon correlation technique to measure the time correlation function of scattered light from polymer solutions. This time correlation function at any momentum transfer,  $q$ , is related to the intermediate scattering function,  $S(q,t)$ , which is a Fourier transform of the space correlation function of monomer pairs. Therefore, in principle, measurement of  $S(q,t)$  can provide not only a measure of the properties associated with the equilibrium distribution of polymer segments such as the radius of gyration,  $R_G$ , or the statistical segment length, but can also measure physical properties associated with the time evolution of polymer segment distributions, such as the hydrodynamic radius,  $R_H$ , or the hydrodynamic interaction strength.

Our most recent efforts have been centered on the development of theories for the intermediate scattering function,  $S(q,t)$ , and the characteristic frequency,  $\Omega(q)$ , for polymer



solutions. Such theories are essential for the interpretation of quasielastic light and neutron scattering data. Our theory includes both temperature and molecular weight dependence specifically. We have also successfully applied this theory to a different characterization technique, intrinsic viscosity.

### Interpretation of Scattering Experiments on Polymer Solutions

A. Z. Akcasu<sup>1</sup>, M. Benmouna<sup>1</sup>, and C. C. Han

Interpretation of dynamic scattering experiments requires, ideally, a theory that can predict the intermediate scattering function,  $S(q,t)$ , and a chain model consistent with the chemical structure of the polymer. Unfortunately, exact expressions of  $S(q,t)$  are available, at present, only for single unperturbed ( $\theta$ -condition) gaussian chains without hydrodynamic interaction (Rouse model), or, in the infinite chain limit, with hydrodynamic interaction and preaveraged Oseen tensor (Rouse-Zimm model). In this sense, a complete interpretation of scattering experiments on polymer solutions is an unsolved problem. By using linear response theory, we have been able to obtain closed form expressions for  $S(q,t)$  of both linear and circular chains for Rouse and Rouse-Zimm cases in the infinite chain limit. Also, we can express  $S(q,t)$  for finite linear chains in the Rouse limit and for circular chains in both Rouse and Rouse-Zimm limits in closed form. All these can be compared with the method of eigenfunction expansion and the method of solving diffusion equations directly. Advantages of our current scheme have been demonstrated. In the case where an exact solution of  $S(q,t)$  can not be obtained, the characteristic frequency,  $\Omega(q)$ , which is the initial slope, and defined by

$$\Omega(q) = -\lim_{t \rightarrow 0} \frac{dS(q,t)}{dt}$$

can be calculated. The temperature and concentration dependence of  $\Omega(q)$  in terms of "blob model" chain statistics can be calculated not only for the intermediate scaling region, but also for the upper and lower transition regions where information about polymer chain parameters such as radius of gyration,  $R_G$ , statistical length,  $a$ , and hydrodynamic interaction,  $B$ , can be extracted.

### Temperature, Molecular Weight, and Concentration Dependence of Chain Dimensions Around $\theta$ -Temperature

S. J. Bai<sup>2</sup>, D. J. Lohse<sup>3</sup>, I. C. Sanchez, and C. C. Han

Chain dimension and the  $q$ -dependence of the single chain scattering function,  $S(q)$ , are being studied at various temperatures and concentrations with different molecular weights by SANS. Experimental results will be compared with various theoretical predictions. The difference between dimensions in dilute solution at the  $\theta$ -temperature and in the bulk state will be studied.

### Concentration Dependence of Diffusion Coefficient at Various Molecular Weights and Temperatures

A. Z. Akcasu<sup>1</sup> and C. C. Han

Experimental results of the concentration coefficient,  $k_D$ , of the diffusion coefficient,  $D$ , of polymers in dilute solution have been investigated and compared with various theoretical predictions. The negative  $k_D$  for small molecular weight and low temperature and the positive  $k_D$  for large molecular weight and high temperature can be understood through model calculations which include chain swelling and intermolecular potential. The molecular weight independent, but negative, concentration dependence of  $D$  at  $\theta$ -temperature indicates the contributions of overlapping pairs of molecules. Chain expansion at the  $\theta$ -temperature due to chain overlap is implied.

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<sup>2</sup>IAP assignment from University of Michigan.

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## Dynamic Structure Factor, $S(q,w)$ , of Dilute Polymer Solutions

A. Z. Akcasu<sup>1</sup> and C. C. Han

Most of the quasielastic neutron and some of the quasielastic light scattering experiments are performed in the frequency domain due to the characteristics and availability of experimental facilities. The extraction of the characteristic frequency  $\Omega(q)$  from  $S(q,w)$  data poses difficulties similar to those in time domain analysis. Although  $S(q,w)$  is just the Fourier transform of  $S(q,t)$ , it is not straightforward to obtain an analytical expression for  $S(q,w)$  even in the cases where  $S(q,t)$  is available. On the other hand, it is not fruitful to perform numerical inverse Fourier transform on the experimental  $S(q,w)$ , due to the finite data set and lack of precision. We have, therefore, investigated the shape of  $S(q,w)$  numerically for various cases to facilitate the extraction of  $\Omega(q)$  from  $S(q,w)$  directly in both light scattering and neutron scattering experiments.

### Domain Structure of Block Copolymers and Characterization of Polyelectrolyte

I. Noda<sup>2</sup>, T. Hashimoto<sup>3</sup>, S. J. Bai<sup>4</sup>, D. B. Minor, and C. C. Han

Preliminary study of the domain interface structure of star shaped polystyrene-polyisoprene block copolymers has been carried out by neutron scattering. Data analysis is in process, and further experiments are in preparation.

Also, the characterization of polyacrylic acid by combined measurement of SANS and LS under various salt concentrations and charge densities is under way.

### Development of a Digital Lock-in Light Scattering Photometer and the Measurement of Polystyrene 1479 and UHMW Polyethylene

D. B. Minor, H. L. Wagner, and C. C. Han

A state-of-the-art light scattering photometer has been developed for the purpose of measuring the molecular weight of polymer SRM's and ultra high molecular weight synthetic implant materials. This photometer, which utilizes photon counting and digital lock in, has been tested by measuring previously certified SRM's.

A temperature controller has been installed and tested for polyethylene measurements at elevated temperatures. Measurement of polystyrene 1479 ( $M_w \sim 10^6$ ) in toluene has been completed for SRM certification. Measurements of ultra high molecular weight polyethylene is currently under way.

### Configurations of Polymer Chains

R. J. Rubin

A review of applications of the theory of random walks to polymer chain configurations is being prepared with G. H. Weiss of the National Institutes of Health. This review also includes a number of new results: 1) a new connection has been established between random walk probability distributions and a generating function obtained by Rubin [J. Chem. Phys., **43**, 2392 (1965)] for calculating configurational properties of a polymer chain attached to an adsorbing (or repelling) solution surface. In particular, Eq. (26) of that paper can be expanded as a power series in  $e^\theta$ . The coefficient of  $e^{s\theta}$  is the probability that a random walk originating in the solution surface layer will return  $s-1$  times to the surface in an  $N$ -step walk. Random walk probability distributions of this type are considered by E. W. Montroll and G. H. Weiss, [J. Math. Phys., **6**, 167 (1965)]. When Rubin's Eq. (26) is viewed in this way, random walk configurations are classified according to the number of visits,  $s$ , to the surface layer. Then the total probability is the sum of the weighted probabilities where the weight function is

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proportional to  $e^{s\theta}$ , a Boltzmann weight factor. 2) The treatment of a polymer chain between two plane solution surfaces given by DiMarzio and Rubin [J. Chem. Phys., 55, 4318 (1971)] has been extended to treat polymer chains of finite length. All the results obtained by DiMarzio and Rubin pertain to the limit in which the ratio of the extended chain length to the separation between the bounding planes is large compared to unity. One quantity of particular interest is the average step density as a function of position between the solution surfaces. For random walks of  $N$  steps, configurations can be classified according to the number of visits,  $r, s$ , to the two solution surfaces. The subclass of  $N$ -step random walks in which each surface is visited at least once is identical to the subclass of  $N$ -step random walks whose span is the same as the distance between the solution surfaces. The calculation of the step density for  $N$ -step random walks with a given span is in progress.

In the absence of the complicating effects of interaction with surfaces, probability distribution functions of configurations of long chain molecules can be modeled by solutions of a random flight or diffusion equation. However, it is known from studies of lattice models that if the energy of attraction between links of the polymer chain and the surface becomes sufficiently high, then there is a discontinuous collapse of the chain on the surface. The description of such discontinuous behavior within the framework of a diffusion equation appears to present technical difficulties.

DeGennes [Reports Prog. in Phys., 32, 187 (1969)] has proposed that the appropriate boundary condition in the case of a "weakly adsorbed" chain is the mixed boundary condition,  $\ell \partial G / \partial x + mG = 0$  at the solution surface, where  $G(x, N)$  is the solution of the diffusion equation. DeGennes drew the analogy between his suggestion for the boundary condition of the diffusion equation and the treatment of the bound state of the deuteron. We have approached the question of the appropriate boundary condition for the diffusion equation in a complementary way. Starting with the lattice random walk equations in Rubin [J. Chem. Phys., 43, 2392 (1965)], we have assumed that not only the surface layer is modified by a factor  $e^\theta$ , but each of the first  $\ell$  layers are modified by this factor. We then go to the random flight limit in which the lattice equations are replaced by diffusion equations.

For this special model, we see how to establish a correspondence between the solution of a diffusion equation with a source (sink) term in an adsorbing (repelling) layer with an absorbing boundary condition and the solution of a diffusion equation with the mixed boundary condition proposed by DeGennes.

### The Characterization of Ultra-High Molecular Weight Polyethylene For Synthetic Implants

H. L. Wagner and J. G. Dillon<sup>1</sup>

The development of new or modified methods for characterizing the molecular weight and molecular weight distribution of ultra high molecular weight polyethylene (UHMWPE) has continued with major emphasis on work on the low shear viscometer. The light scattering apparatus has been readied for high temperature operation, and a new fractionation bath is being assembled.

Because of problems with wobble of the rotor and poor reproducibility, major modifications were made in the viscometer design. As a result of these changes, it is now possible to reproduce solvent readings to within one percent, and the wobble of the rotor is no longer noticeable at those periods of rotation required for viscosity number determinations.

A problem remains with reproducibility for solutions of UHMWPE which appears to be due primarily to solution preparation. If severe enough means are not employed to dissolve the polymer, complete solution is not obtained. If too severe a method is used, on the other hand, degradation occurs. Considerable effort has gone into finding a satisfactory technique, and a promising one is now being evaluated. It consists of heating the solution at 150 °C under nitrogen for one hour with just enough gentle swirling to keep the polyethylene particles separated before melting. This avoids the formation of globs which are very difficult to dissolve.

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<sup>1</sup>Guest worker, Food and Drug Administration.

Viscosity values in decalin in the low shear viscometer are some twenty percent higher than in tetralin, a surprising result, since if the Mark-Houwink equations (evaluated for lower molecular weights) are extrapolated to higher molecular weights, very similar viscosity numbers would be expected for these solvents. It is also found that these high values in decalin decrease at the rate of two to three percent per hour for the first few hours, a change which does not occur with tetralin or with either solvent in the ordinary capillary viscometer, which operates at much higher shear rates. Whether these differences are due to degradation or some other phenomenon has not been determined.

Once the technique for obtaining low shear viscosity numbers is established, fractionation will begin in order to obtain fractions for establishing the Mark-Houwink equation for UHMWPE.

### Cell Model Theory of Polymer Solutions

I. C. Sanchez and D. J. Lohse<sup>1</sup>

An incompressible, statistical thermodynamic theory of a polymer solution is formulated which takes into account concentration inhomogeneities. A generalized cell model is used as the basis for the new polymer solution theory. Closed-form, parametric equations are obtained for solvent and polymer chemical potentials which only reduce to classical (Flory-Huggins) potentials when concentration homogeneity is assumed. In a good solvent, the calculated second virial coefficient decreases with molecular weight ( $M^{1/5}$  dependence) in good agreement with available experimental data. In dilute solutions, chain dimensions can be analytically determined; the well-known Flory excluded volume equation is obtained. The most important parameter in the cell model is the average number of chains/cell,  $\lambda$ . For semi-dilute solutions ( $\lambda \gg 1$ ), it is shown that several important scaling results are recovered from a simple scaling hypothesis for  $\lambda$ .

### Interfacial Tension Theory of Low and High Molecular Weight Liquid Mixtures

I. C. Sanchez and C. I. Poser<sup>2</sup>

A generalized van der Waals or density gradient theory of interfaces has been combined with a compressible lattice theory of homogeneous fluid mixtures. Binary liquid-vapor and liquid-liquid systems are treated. For non-polar low molecular weight mixtures, liquid-vapor tensions are calculated as a function of composition with an error of less than five percent. These calculations involve no adjustable parameters; all required parameters are determined from pure component properties. For polymer solutions, it is usually necessary to introduce an adjustable interaction parameter to accurately correlate liquid-vapor tensions. Approximate equations for the interfacial tension and thickness between two immiscible, high molecular weight polymer liquids have been obtained. These equations are a function of a single interaction parameter; when this parameter is chosen to match experimental tensions, interfacial thicknesses of 1 to 5 nm are obtained. To assess the importance of compressibility effects, the interaction parameter can be chosen so that the heat of mixing is zero for an incompressible system. This "pure compressibility approximation" works well for polymer pairs with relatively low interfacial tensions. The most serious deficiency of the theory is that intramolecular correlational effects present in long polymer chains are only crudely approximated.

### Configurational Properties of Comb-Branched Polymers

F. L. McCrackin and J. Mazur

Mean-square radii of gyration were computed for comb-branched polymers simulated on a cubic lattice by chains with both excluded volume and attractive energies between nonbonded segments of the polymer. The ratios,  $g$ , of the radius of gyration of a comb-branched polymer to that of a linear polymer of the same molecular weight at the theta point were found to be larger

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than the g ratios calculated by the unrestricted random-walk model of the polymer. These calculated g ratios showed better agreement with experimental measurements than did those calculated by the random walk model.

The radii of gyration of the backbones and the expansion factors of the comb-branched polymers were also calculated. The radii of gyration of the backbones at the theta condition were greater than that of linear polymers, in contradiction to the random walk model which requires that they be equal. The calculated expansion factors were less than that of linear polymers, also in contradiction to the random walk model.

### Rubber and Rubber Compounding Standard Reference Materials

G. W. Bullman and G. B. McKenna

The process of streamlining the NBS Rubber Program is continuing in response to reduced resources available for this program. As part of this reduction, rubber and rubber compounding Standard Reference Materials, for which NBS serves primarily as a warehouse facility, are being removed from the SRM list as inventories are exhausted. In addition, several materials are being removed from the list due to poor sales. These SRM deletions are being coordinated with ASTM Committee D-11 on Rubber and Rubber-like Materials and Committee D-24 on Carbon Black to assure an orderly change in the ASTM standards and within the rubber industry.

In order to serve industry's needs for rubber SRM's with our reduced resource base, we are maintaining inventories of materials which industry (through ASTM) has indicated are important, even though NBS's primary function for these materials is to serve as a warehousing facility. For example, we are recertifying N-tertiary-butyl-2-benzothiazole sulfenamide [SRM 381(d), a rubber accelerator] in order to maintain inventories of this material. In addition, where standards involve certification of basic physical properties, we are assuring the renewal of the SRM's as necessary, and where the need is indicated, we are issuing new SRM's. Thus, last year we recertified the butyl rubber SRM 388(k) which is used as a Mooney Viscosity Standard. During this year, we have completed the work necessary for procurement of a new Mooney Viscosity Standard, thus extending the range of Mooney Viscosity Standards available to the rubber industry.

### Collapse Transition of the Isolated Polymer Chain

I. C. Sanchez

A mean field theory of chain dimensions has been formulated which is very similar to the van der Waals theory of a simple fluid. In the limit of infinite chain length, the chain undergoes a second-order phase transition. At low temperatures, the chain is in a condensed or globular state, and the mean square gyration radius  $\langle S^2 \rangle$  varies as  $m^{2/3}$  where  $m$  is the molecular weight. At high temperatures, the chain is in a gaslike or coil state where  $\langle S^2 \rangle$  varies as  $m^{6/5}$ . In the globular state, fluctuations in  $\langle S^2 \rangle$  are very small, whereas they are very large in the coiled state. A characteristic feature of the theory is that ternary and higher order intramolecular interactions are approximated. At high temperatures, only binary interactions are important, but at low temperatures, many of the higher order terms contribute. An important conclusion of this study is that a polymer chain does not obey ideal chain statistics at  $\theta$  temperature. Although the second virial coefficient vanishes at  $\theta$ , the third virial coefficient does not; its presence is responsible for the perturbation of the chain statistics. For an infinite chain,  $\theta$  and the second-order phase-transition temperature are identical. When generalized to  $d$  dimensions, the theory yields at low temperatures  $\langle S^2 \rangle^{d/2} \sim m$  for all  $d$  and at high temperatures  $\langle S^2 \rangle \sim m^{6/(d+2)}$ ,  $d < 4$ , and  $\langle S^2 \rangle \sim m$ ,  $d > 4$ .

L. E. Smith

Task Leader

Polymeric materials now find their principal markets in construction, appliances, transportation, and electrical systems where long term durability is critical to their competitive performance. Reliable short term tests are therefore needed for the selection of durable polymers and knowledge of polymer degradation mechanisms is needed to guide the development of protective methods and to improve performance. Technical work this year has emphasized the determination of the mechanism of degradation and stabilization of polyurethanes, the use of thermogravimetric measurements for lifetime prediction, and the development of chemiluminescence methods for the detection of photoinitiated oxidation in polymers.

The most general phenomenon related to the durability of polymers is the effect of protective additives. Almost all commercial plastics have low molecular weight substances incorporated in them to develop or maintain desirable properties. In use, these substances 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 increased vulnerability to degradation and failure. This is a major failure mode of polymers, and programs concerned with polymer durability must explicitly consider the possibilities of additive migration. A second consequence of migration is that the migrating substance becomes a contaminant of the environment or, in the case of plastic packaging materials, a contaminant of the material being contained. This raises questions about the toxicological consequences of such migration. Contamination of food from food packaging materials is regulated by the federal government through the Food and Drug Administration, and the control of migrating substances presents an enormous challenge to the scientific basis of regulations.

The number of commercially usable polymer-additive combinations is too large to be considered efficiently on a case by case basis, either for selection of materials of optimum durability or for regulation of food and environmental contamination. General material models capable of predicting migration under a variety of service conditions are needed to organize polymer-additive combinations into classes for consideration. The development of these material models is the overall objective of work done in this task.

Technical activities on additive migration that contribute to this task include 1) the experimental measurement of additive migration by several methods, 2) the compilation of critically evaluated data from this laboratory and the literature, 3) mathematical modeling and empirical correlation of diffusion data for analysis of data and rapid estimation of migration, and 4) fundamental theoretical studies of polymer behavior that can provide truly general predictive models.

#### Hydrolytic Degradation of Polyester Polyurethane Elastomers

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

Polyester based polyurethanes degrade in moist air because of the acid catalyzed hydrolysis of the ester linkages [1]. With soluble polymers, acid content,  $A$ , and number average molecular weight,  $M$ , vary with time,  $t$ , according to [2]:

$$A = A_0 e^{kt} \text{ and } M^{-1} = M_0^{-1} + A_0(e^{kt} - 1)$$

Here the subscripts indicate initial values, and  $k$  is the fractional rate of increase in acid content.

These findings were applied to the study of insoluble urethane foams used in the fuel cells of military aircraft [3]. Foam samples were aged until soluble. Subsequent agings then enabled us to calculate  $k$ , which permitted prediction of the remaining foam life. A test using swelling in dimethylformamide was developed that permits one to judge very quickly the condition of foam in existing installations.





- (1) it is able to determine activation energy using only one sample so that problems arising from differing thermal histories of two or more samples are avoided,
- (2) several activation energies are determined in each experimental run so that changes in sample behavior can be discerned,
- (3) because the activation energies are determined from locally extrapolated rates, no knowledge of the initial and final sample weights is necessary, and
- (4) automatic feedback adjusts the experimental conditions for changing sample behavior. Points 3 and 4 allow the method to treat multi-stage degradations successfully.

The results of thermogravimetric experiments conducted on several polymers under vacuum conditions were fairly erratic and difficult to interpret. Although it is generally difficult to determine whether the instability results from the apparatus or the method, it has now been shown convincingly that a large part of the variation is in the thermal history of the sample. Only in the cases of polymers degrading with very long zip lengths to produce mainly monomer could results of chemical rather than physical significance be obtained in vacuum. The most fiducial results for all polymers studied so far have been in slowly flowing  $N_2$ , but even there the experimental conditions play a surprisingly large role. For isotactic polypropylene, the apparent activation energy for thermal degradation in vacuum was determined to be  $61.5 \pm 0.8$  kcal/mole; for linear polyethylene it was  $65.4 \pm 0.5$  kcal/mole. In slowly flowing  $N_2$ , the apparent activation energy is  $54 \pm 1$  kcal/mole for isotactic polypropylene and  $51.5 \pm 0.5$  kcal/mole for atactic polypropylene. For linear polyethylene, the value is  $61 \pm 1$  kcal/mole. These values are significantly different from the vacuum values and from most of the published values. In the case of polypropylene, a reasonably careful study carried out elsewhere assigns  $56 \pm 5$  kcal/mole to atactic polypropylene and  $51 \pm 5$  kcal/mole to isotactic polypropylene. Those results are 5-10 times more imprecise than the results from factor-jump thermogravimetry. We will continue to use the factor-jump thermogravimetry technique to study the effects of experimental conditions, molecular weight, and branching on the activation energy of thermal degradation of polypropylene, polyethylene, and several other polymers.

Computer programs have been written to drive the apparatus and to conduct various statistical tests to provide estimates of the precision of the results and to reduce as much as is feasible the effect of aberrant values. These programs and procedures have been documented in a User's Guide.

### Variable Heating Rate Thermogravimetry

J. H. Flynn

The prediction of the lifetime of a polymer by extrapolation from weight-loss data requires a thorough analysis of the degradation kinetics over a wide temperature range. Techniques have been developed in which entire kinetic spectra are compared among experiments performed at heating rates from 6 deg/min to 9 deg/day. Simple methods of plotting data from these techniques have been used for diagnosing shifts in reaction mechanism, uncoupling of competing processes, and testing the validity of kinetic models.

Weight-loss studies are continuing on polystyrene, poly(methyl methacrylate), and polyurethanes in vacuum and in atmospheres containing nitrogen, air, and water vapor. Subtle changes in mechanism have been exposed for several of these cases under the milder conditions of the above techniques. It now appears that rapid conventional thermogravimetric techniques at high temperatures are inappropriate for the prediction of service lifetime of these polymers.

### Chemiluminescence From Oxidizing Polymers

R. E. Florin and B. Dickens

Polymers emit light weakly during oxidation. This effect has aroused recent interest as a means of monitoring oxidative deterioration of polymers. A widely accepted theory of the effect is that the light is emitted during the termination step of the oxidation chain reaction. Although the quantum yield of light emission is estimated to be only one photon per  $10^9$  terminations, this inefficiency can be overcome by the technique of counting individual



photons, which leads to an extremely sensitive method, potentially capable of detecting oxidation at temperatures only a little above those of normal service. In contrast, more accelerated aging methods require a long extrapolation from high test temperatures to service temperatures, and the mechanism of degradation probably changes.

The general objective is to obtain a representative data base for correlating chemiluminescence emission rates with overall oxidation rates for polymers of differing physical and chemical characteristics. The appropriate kinetic parameters are the rates of initiation, propagation, and termination. We have devised a method for measuring one of the individual rate constants of the process, that of termination. A prototype photon counting apparatus has been constructed. Ultraviolet light activates a photoinitiator solute which then attacks the solvent which may be polymer, rubber, or liquid. The light can be cut off suddenly, and decay in the oxidation rate followed to give estimates of the rate constants of the termination reaction. Oxidations initiated thermally, without irradiation by light, give estimates of the rate of initiation of polymer oxidation itself, i.e., the rate of transfer from the initiator to the polymer. This is because under these conditions the polymer oxidation is a chain reaction operating in the steady state, and the rate of initiation is equal to the rate of termination.

Evaluation of transfer of radicals from the photo-initiator to the polymer provides essential information on the dispersion of the initiator in the polymer and also allows us to study the influence of the "cage effect" on the initiation process. Evaluation of the termination rate constant under various conditions allows us to study the influence of the cage effect on the termination process. One example of the cage effect is when two radicals, newly produced adjacent to one another by a bond-breaking process, are held in close proximity to each other by the matrix and react with one another without attacking their environment. If a radical escapes from the cage, it continues the polymer oxidation process until it reacts with either another similar radical or an added radical-trapping molecule. Effects of cages bring severe complications in the understanding of oxidation and are poorly characterized.

The chemiluminescence will also be used to study initiation by sensitive groups on the polymer, such as the ROOH groups produced during oxidation under normal conditions. Other parameters needed to complete the characterization of the oxidative chain reaction are the kinetic chain length and the total amount of oxidation. These can, in principle, be determined with techniques already described in the literature. However, to achieve sensitivity useful at the low levels of oxidation at which the chemiluminescence photon counting method gives useful information, these literature techniques will need further development.

The extreme sensitivity and very low levels of light emission bring their own problems. Extreme care was necessary to produce a sample enclosure with a level of luminescence low enough for the sample to be "seen". There are problems in dissolving enough photoinitiator in polymers without precipitating it as a second phase. Also, careful measurements have shown that oxidation phenomena are not as simple as they are usually thought to be.

The procedure described here is now highly automated, the apparatus being controlled by a laboratory computer. The existence of spikes of high counts (cause unknown) and of zero or very low counts from occasional non-opening of the shutters required the writing of a trimmed-mean estimating program. Other programs provide needed processing of data and continuously update the level of photoinitiator left in the sample.

Currently, the optimum technique is being developed, and calibrating runs are being carried out on simple organic compounds for which the termination rate constants are known. The procedure and programs developed up to now are being documented in a User's Guide.

#### Migration of Oligomers and Antioxidants From Polyolefins

S. S. Chang, W. J. Pummer, J. R. Maurey, and L. E. Smith

During the last two years, a rather thorough experimental investigation of the kinetic behavior of the migration of oligomers and antioxidants from polyolefins into food and food-simulating solvents has been carried out. This program is under the sponsorship of the Food and Drug Administration. Extractions of migrants by actual foods are being carried out by a separate FDA contract at Arthur D. Little, Inc. The only food used in the program here is the corn oil, for the purpose of finding some solvents that simulate the extracting action of food oils.



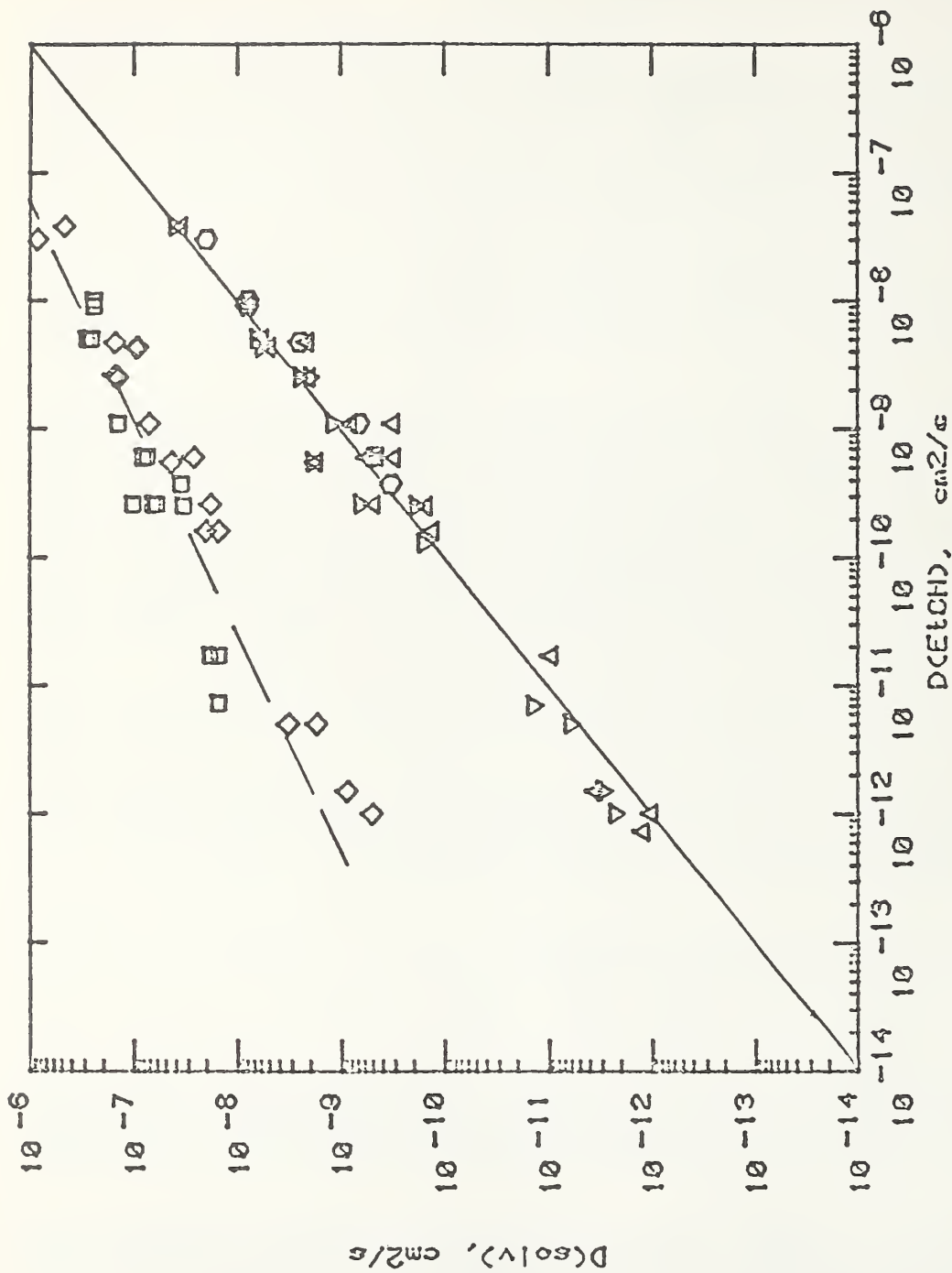


Fig. 1. Apparent Diffusion Coefficient of Migrants in Different Solvents  
 —  $\Delta$  corn oil,  $\circ$  tributyrin, and  $\nabla$  trioctanoin versus ethanol  
 — n-heptane versus ethanol ( $\diamond$  oligomers,  $\square$  BHT)

Variations included in each of the correlations:

- Polyolefins - linear and branched polyethylenes and isotactic polypropylene
- Migrants -  $n\text{-C}_{18}\text{H}_{38}$ ,  $n\text{-C}_{32}\text{H}_{66}$ , and BHT
- Migrant Concentrations - 0.001 percent to 10 percent
- Temperature - 24, 30, and 60 °C

A large number of experimental variables have been investigated. These variables are 1) polymers--linear polyethylene, branched polyethylene, and isotactic polypropylene; 2) migrants-- $n\text{-C}_{18}\text{H}_{38}$ ,  $n\text{-C}_{32}\text{H}_{66}$ , and BHT; 3) solvents--corn oil, tributyrin, trioctanoin, ethanol, ethanol-water mixtures, water,  $n\text{-heptane}$ , and  $n\text{-octadecane}$ ; 4) temperature--30 and 60 °C. Furthermore, the initial concentrations of the migrants in the polymers and the thickness of the sample plaques have also been varied. Besides the kinetic studies, equilibrium properties such as solubilities and partition coefficients have also been studied. The migrants used are labeled with radioactive  $^{14}\text{C}$ , to yield a detectibility of  $10^{-10}$  g if needed. The extraction experiments generally require a few weeks to a few months to complete; however, some experiments are completed within a few days, while some may last longer than a year.

There are about two hundred extraction experiments scheduled. Most of these experiments are now completed. The diffusion coefficients observed vary from near  $10^{-6}\text{cm}^2\text{s}^{-1}$  to less than  $10^{-15}\text{cm}^2\text{s}^{-1}$ . Some of the experiments indicate an ideal Fickian behavior, especially for pre-swollen polymer in one extreme and for non-swelling solvents in the other extreme. For the intermediate cases, the diffusion coefficient may increase from an initial value and then level off at a higher value or may increase drastically, such that the migrant is exhausted before seeing the leveling off of the diffusion coefficient at a higher value.

From these results, certain generalizations and correlations can be drawn for the migration of oligomers and antioxidants from polyolefins. These findings may form a basis for the estimation or prediction of the diffusion coefficients in situations not mentioned above.

If all other parameters are held constant, then it seems that the ranking of importance for the parameters on the diffusion coefficient of migrants from polyolefin is as follows: solvent, temperature, additive type, polymer type, additive concentration. The first three parameters are far more important than the remaining two. There are overlapping cases of the ranking at the extremes of these parameters.

#### Effect of Solvent

Solvent is the single most important parameter in the correlation scheme. For moderate solubilities, e.g., above one percent, one may make correlation of the diffusion coefficients only to the solvents irrespective of other variables such as polymers, additives, additive concentrations, and temperatures. Figure 1 shows the correlations of diffusion coefficients in several solvents versus that in ethanol, while other variables being kept identical. Although by changing solvents the diffusion coefficients may change by a factor of more than 2000, the simple correlations indicated in Figure 1 can reduce the variation down to a factor of 3 or less. The two correlations shown are for  $n\text{-heptane}$ , and for the combination of corn oil, tributyrin, and trioctanoin.

The diffusion coefficients in corn oil, tributyrin, and trioctanoin are nearly identical to that in ethanol within a factor of 3. The ratios of diffusion coefficients among the two pure triglycerides and the corn oil are in general less than 1.5. Therefore, either ethanol, tributyrin, or trioctanoin can be used to simulate the extractive action of corn oil in a great variety of conditions involving different additives, polyolefins, and temperatures.

The accelerated action of  $n\text{-heptane}$  over that of the corn oil or its equivalents is clearly demonstrated in Figure 1. The diffusion coefficient is only 10 to 20 times higher in the case of high diffusion coefficients, such as in the case of highly loaded  $n\text{-C}_{18}\text{H}_{38}$  in branched polyethylene at 60 °C. However, the disparity increases as the diffusion coefficient is decreased, as may be seen in other correlations with temperature, etc. Thus, for the case of extracting higher molecular weight oligomers,  $n\text{-C}_{32}\text{H}_{66}$ , from linear polyethylene at 30 °C, the diffusion coefficient in  $n\text{-heptane}$  is about 1000 times higher than that in corn oil or its equivalents.

Combining the effects of the accelerating action and the greater solubility of  $n\text{-heptane}$  over that of ethanol for polyolefin oligomers, the extract of the whole polymer by  $n\text{-heptane}$  contains a large amount of higher molecular weight oligomers that may be barely present or absent in the ethanol extract under the same conditions.

When the solubility is low, e.g., in the cases of using ethanol-water mixtures or water as solvents, it is difficult to make simple correlations as a function of solvent without taking

other variables, such as polymers, additives, partition coefficients, and temperatures, into account.

### Effect of Temperature

Similarly, diffusion coefficients for additive migration at 30 °C may be correlated to the diffusion coefficients at 60 °C by a single relationship to a factor within 5, irrespective of all other variables. Again, the effect is minimized at higher diffusion coefficients and increased at lower diffusion coefficients. Better correlations can be made by separating other variables such as additives and polymers. The activation energies observed range from 20 kJmol<sup>-1</sup> to 200 kJmol<sup>-1</sup>.

### Effect of Additive

Changing of additives while keeping all other variables the same also changes the diffusion coefficients drastically. It is not possible to construct a simple correlation with respect only to the additives but irrespective of all other variables. Reasonable correlations may be made for additive-polymer combinations. Even then, definitive structures in the correlations due to solvent or temperature are observed.

### Effect of Polymer

For all cases studied, the diffusion coefficient changes, at maximum, by a factor of less than 50 due to the changes from low crystallinity branched polyethylene to high crystallinity linear polyethylene and isotactic polypropylene. Fine correlation requires other variables such as additive and temperature to be kept constant.

### Effect of Additive Concentration

If the additive, such as BHT, is insoluble in the polymer or does not act as a plasticizer, no significant effect on diffusion coefficients due to the change in additive concentration has been observed. Changing the concentration of n-C<sub>18</sub>H<sub>38</sub> from one percent to 0.01 or ten percent may produce a change in the diffusion coefficient by a factor of 40 in the cases studied. Correlations as a function of concentration for a particular additive but irrespective of other variables are possible.

### Conclusion

From the above observations, one can make a reasonable order of magnitude estimate of the diffusion coefficient if any of the variables such as solvent, temperature, polymer, and additive concentration is changed, while the estimation of the effect of changing of additives without specifying other conditions would be rather difficult.

## A Critical Compilation of Data on the Diffusion of Additives in Polymers

J. H. Flynn

The compilation of kinetic constants for the diffusion of organic compounds in polymeric materials will result in a reliable data base which may be utilized both to evolve theoretical models for diffusion mechanisms and to establish empirical relationships for the prediction of the migration of chemicals and additives in polymers used in the food packaging, chemical container, and transportation industries. With support from the Office of Standard Reference Data, a comprehensive collection of kinetic data on the diffusion of organic compounds in polyolefins has been completed and prepared for publication.

The tables for low density polyethylene, high density polyethylene, polyisobutylene, polypropylene, hydrogenated polybutadiene, poly(4-methylpentene-1), ethylene-propylene copolymers, and self-diffusion of polyolefins contain over 250 polymer-migrant entries. Diffusion constants at temperatures from -30 to 190 °C, activation energies and preexponential factors for the diffusion process and parameters for the concentration dependence of the diffusion constant are included.

A special feature of this compilation is an extensive section of annotated references. These include: 1) as complete a characterization of each polymer and migrant as is possible, 2) a description of the experimental methods used to determine the diffusion constants, and 3) the



assumptions made, equations utilized, and calculations performed to obtain the data in the tables. The justification for this lengthy section is twofold. The large effects of structure and conditioning of the polymer substrate on the diffusion process require a detailed description of the characterization and pretreatment of the polymers if the data are to be compared and their differences interpreted. Secondly, since diffusion constants are a function of time, concentration, and distance, a knowledge of the experimental conditions, methods of measurement, and theoretical models evoked for the calculations is also essential for an understanding of the data.

The tables exhibit remarkable consistencies, considering the great variations in diffusion constants which can be brought about by thermal, mechanical, and solvent action. These consistencies lend hope that useful correlations may be developed from these data.

Work has begun on a similar compilation of kinetic data for the diffusion of organic migrants in polystyrene--a polymer of commercial and theoretical importance--which in contradistinction to the polyolefins, is in a physical state below its glass transition temperature at normal service temperatures where most of the diffusion data on it have been obtained.

### Measurement of Migration in Polymers by Inverse Gas Chromatography

G. A. Senich

Inverse gas chromatography (IGC) is being evaluated as a method for studying the thermodynamic and kinetic interactions of volatile compounds or probes with polymers. The experimental procedure is similar to conventional gas chromatography with the exception that a solid or molten polymer replaces the usual liquid stationary phase. Low carrier gas flow rates insure that the probe retention time is sufficiently long for a steady-state distribution between the vapor and polymer phases to be established. The specific retention volume  $V_g^0$ , a measure of the thermodynamic interaction between the probe and polymer, is then determined from the total amount of carrier gas necessary to elute the probe from the column. Experiments with alkanes and well characterized NBS polyethylene samples have been performed both above and below the polymer melting temperature. The  $V_g^0$  values determined above the melting temperature agree with results in the literature derived for similar systems. An error analysis has been effected to establish the precision which can be expected for such experiments. Since the amorphous fraction is the sole contributor to bulk sorption of the probe molecules below the melting temperature, the accuracy to which the percent crystallinity is known limits the reliability of determinations in this temperature region. The polymer-probe interaction parameter has been calculated from  $V_g^0$  by applying relations derived from the equation of state based polymer solution theories of Flory and of Sanchez and Lacombe, both yielding similar results. This parameter can be used to predict a limiting value of the partition coefficient, which describes the distribution of the probe between a polymer and a non-swelling liquid in contact with it, provided that the solubility of the probe in the liquid is known to be small.

The migration kinetics of a probe in the polymer phase can be related to the degree of broadening of the eluted probe pulse over its initial injection distribution. At high carrier gas flow rates, there is insufficient time for the probe to reach a steady-state distribution between vapor and polymer phases. The degree of peak spreading is related to the rate of mass transfer occurring in the column, provided that contributing instrumental factors, such as dead volume, are negligible. The magnitudes of various gas phase mass transfer processes have been estimated and their effects minimized in a series of studies on diffusion of octadecane in polyethylene. The diffusion coefficient has been determined for this system and found to be extremely sensitive to the geometry of the polymer film present on the spherical support particles. Knowledge of the film thickness distribution, in addition to its average value, is critical to the experimental determination of reliable diffusion coefficients by IGC. Future work will include studies of diffusion in polymer systems with clearly defined geometry. IGC experiments on diffusive processes in glassy polymers will also begin.

## Diffusion Coefficient of Medium Size Molecules in Semicrystalline Polymers

A. Peterlin and F. L. McCrackin

An empirical correlation of the diffusion coefficient of a number of molecules with sizes between  $N_2$  and  $SF_6$  in natural rubber and in polyethylenes of increasing crystallinity can be given by

$$D' = KD^m$$

where  $K$  and  $m$  depend on the polymer but not on the penetrant. The diffusion coefficients are given by this expression within a relative error of 4.7 percent. This expression may be interpreted in terms of the fractional free volume,  $f$ , concept of the material transport. According to this model, the diffusion coefficient is given by

$$D = A \exp(-B/f)$$

where  $B$  depends on the size and shape of the penetrant molecule while  $f$  and, to some extent  $A$ , depend on the particular polymer. By introducing this expression for  $D$  and  $D'$ , one obtains  $m = f/f'$ , which permits the calculation of the ratio of the fractional free volume in the polymers investigated. For the cases investigated,  $f$  of the amorphous component, which is responsible for practically all the material transport, depends substantially on the crystallinity. At the highest observed crystallinity of 0.77, the fractional free volume seems to be only 67 percent of the fractional free volume in polymer with the low crystallinity of 0.29. The situation is still more extreme if one includes natural rubber which does not contain any crystals. Polyethylenes with crystallinity 0.77, 0.43, and 0.29 have a fractional free volume which is 0.58, 0.76, and 0.86, respectively, of the fractional free volume of the purely amorphous natural rubber.

### Measurement of Antioxidant Migration by Fluorimetry

F. W. Wang

The migration of antioxidants from polymer films is being studied by extraction experiments. In an extraction experiment, a plane sheet of polymer with uniform concentration of an antioxidant is immersed in a limited amount of well-stirred solvent. Then, the amount of the antioxidant extracted by the solvent is determined at various times by fluorimetry.

Experiments were performed to measure the extraction on  $N,N'$ -diphenyl- $p$ -phenylene-diamine (DPPD) by heptane at 22.0 °C from 0.27 mm thick low-density polyethylene films containing  $8.4 \times 10^{-3}$  percent DPPD. The results showed that all the DPPD had been extracted out of the films within four hours and that the plots of the weight of DPPD extracted against the square root of time were sigmoidal and non-Fickian. These results and others to be collected will be compared with the predictions of a theory being developed by Dr. F. L. McCrackin.

### Excimer Fluorescence Technique for the Study of Polymer-Segment Mobility

F. W. Wang and R. E. Lowry

The study of polymer-segment mobility is of practical as well as scientific interest. Such a study will on the one hand contribute to the design of polymeric reagents and on the other hand, shed some light on "internal viscosity", an idea introduced by Kuhn some 35 years ago and yet still argued about [1,2]. Therefore, we initiated a program to measure polymer-segment mobility by a novel technique based on excimer fluorescence.

An excimer is formed by the association of an excited molecule with another molecule in its ground state. Such an excimer is characterized by a broad structureless fluorescence which is shifted to longer wavelengths with respect to the fluorescence spectrum of the isolated molecule. Similarly, excimer formation may take place by intramolecular processes in polymers carrying excimer-forming groups. Thus, excimer fluorescence has been observed in dilute solutions of polymers such as polystyrene, polyvinyl-naphthalene, and poly(1-naphthyl methacrylate).



We synthesized a random copolymer of methyl methacrylate and 1-pyrenylmethyl methacrylate as well as a random copolymer of methyl acrylate and 1-pyrenylmethyl acrylate, the mole fractions of pyrene-labeled monomers being 0.05 and 0.03, respectively. We then measured the fluorescence spectra for dilute degassed solutions of these polymers at 22.0 °C in ethyl acetate and in mixtures of ethyl acetate and glycerol tripropionate, which have the same chemical nature but different viscosity.

For a given polymer, the value of  $I_D/I_M$ , the ratio of the fluorescence flux emitted by pyrenyl excimers to that by isolated pyrenyl groups, depends on polymer conformation as well as the rate constant  $k_a$  for the diffusion-controlled association of an excited pyrenyl group and a ground-state pyrenyl group to form a pyrenyl excimer. However, by using mixtures of solvents of the same chemical nature but different viscosity, we were able to study the effects of solvent viscosity on  $I_D/I_M$  without modifying the polymer conformation to any significant extent. Thus, at the low enough temperature of our investigation, the ratio  $I_D/I_M$  at photostationary conditions was proportional to  $k_a$  [3]. Since  $k_a$  in turn depends on the polymer-segment mobility, measurements of  $I_D/I_M$  as a function of solvent viscosity allowed us to determine the effects of solvent viscosity on the polymer-segment mobility.

We found that the experimental curves of the reciprocal of  $I_D/I_M$  (or equivalently the reciprocal of  $k_a$ ) against the solvent viscosity were concave downwards. This finding agrees with Cerf's proposal [4] that the highly diversified segmental motions of linear polymer chains belong mainly to two classes which follow diffusional and non-diffusional behavior, respectively, and which may coexist, the former having the reciprocal of the characteristic rate constant proportional to the solvent viscosity and the latter having the reciprocal of the characteristic rate constant a linear function in the solvent viscosity with a non-zero constant attributed to "internal viscosity".

Additional experiments will be performed to study the variation of polymer-segment mobility with polymer structure, solvation of polymer, and polymer-polymer stereocomplex association.

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#### Assessment of Transport Mechanisms for Radon in and Through Building Materials

R. J. Rubin

Accumulation of radioactive radon gas in buildings poses a health hazard. High levels of radon are encountered in certain "hot" geological areas where it emanates naturally from the ground. Certain building materials, such as gypsum board, also contain higher than average amounts of radon. Under an interagency agreement with the EPA, NBS has very recently undertaken the task of studying radon transport in building materials. It involves a cooperative effort between three NBS Centers: Radiation Research, Building Technology, and Materials Science. The initial phase of this project is to critically assess the current state of knowledge of radon transport through or emanation from building materials. The Polymer Science & Standards Division's role is to assess current transport mechanisms and models.



B. M. Fanconi

Task Leader

Current trends are to use polymeric materials in applications where long term mechanical reliability is critically important. Examples in areas of national concern include the increasing use of plastics and composites in transportation, in energy production, storage and distribution, and in medical implant devices. The lack of adequate test methods and data for evaluating long term mechanical performance not only restricts applications, but also leads to overdesign which results in more expensive items and limits potential weight savings. The National Bureau of Standards has established joint programs on mechanical durability with other federal agencies which are fostering the application of polymeric materials in areas of national concern. A joint program with the National Heart, Lung, and Blood Institute is aimed at developing accelerated test methodologies for evaluation of candidate biocompatible elastomers for use as bladders in circulatory assist devices. The Bureau of Medical Devices of the Food and Drug Administration supports an investigation of the relationships between the fine structure morphology of ultra high molecular weight polyethylene and the long term mechanical properties of this material when used in medical implant devices. The mechanical performance of elastomeric seals in geothermal energy wells is of concern to the Department of Energy, and a joint effort is aimed at developing tests to estimate accurately the long-time behavior of seals in any condition of interest. In all of the above applications, there exists a need for test methods and standards to ascertain the physical limits of polymeric materials in various use environments. An outgrowth of a recent project with the Department of Transportation on the mechanical durability of plastic shipping containers has been the development of a new test for environmental stress cracking. This test has been reported to ASTM for evaluation as an improved standard method for stress-crack resistance.

Evaluation and control of materials parameters which affect long-term performance should lead to more durable materials and, hence, reliable performance for the intended service life. Task objectives are to identify and analyze principal failure mechanisms in polyethylene and elastomers under mechanical stress in the use environment. An integral part of these objectives is to determine the effects of chemical structure and mechanisms and fine structure morphology on mechanical properties. Activities in nuclear magnetic resonance, vibrational spectroscopy, electron and optical microscopy, as well as x-ray diffraction, are directed towards elucidating these effects.

#### Mechanical Durability of Polyethylene

J. M. Crissman, L. J. Zapas, and G. M. Martin

In previous work done for the U.S. Department of Transportation, Office of Hazardous Materials Research, a failure mechanism was identified which is highly sensitive to the presence of a stress-cracking agent. This mechanism is associated with the region of small deformations. In an effort to obtain a better understanding of this mechanism, experiments have been carried out on prestretched specimens. In the case of equal biaxial deformations under inflation, the interesting result is that this mechanism is highly influenced by the magnitude of the prestretch history and in such a way that the material becomes more stress-crack resistant. For example, a tenfold increase in lifetime was observed for specimens which were prestretched in air by twenty-five percent, were then left to relax, and subsequently were reloaded in the presence of stress-cracking agent. The eventual failure occurred at strains of twelve percent or less. After prestretching, the permanent set in the specimen was of the order of five percent or less. In all cases where the amount of prestretch was higher than the strain at failure, a significant increase in lifetime was observed. Further investigation is needed in order to understand this interesting behavior. In the case of uniaxial strain histories, the results of similar experiments were inconclusive.

In other work related to mechanical durability studies, we have shown that the phenomenon of neck formation, which occurs for uniaxial deformation histories, can be described by a mechanism leading to instability. Two different theoretical models (phenomenological) have been derived which lead to such an instability. To test the validity of either model, we have chosen for study two types of linear polyethylene having widely different molecular weights. One sample, having a molecular weight ( $M_w$ ) of 192,000, exhibits necking at room temperature.

The other polymer, an ultra high molecular weight material ( $M_w > 2 \times 10^6$ ) does not show necking at room temperature, but extends homogeneously until fracture occurs. In both theories one should be able to predict from single step stress-relaxation experiments, carried out at different levels of strain in uniaxial extension, whether or not an instability occurs. Measurements made at very small deformations indicate that the behavior of the two polyethylenes is very similar. However, at deformations above eight percent, deviations in behavior occur which are consistent with both theories. Data have also been obtained for specimens of highly cross-linked polyethylene which have a density very close to that of the ultra high molecular weight linear polyethylene. The cross-linked material does show the phenomenon of necking. Therefore, experiments other than mechanical will be required in order to elucidate the differences between the two polymers and may lead to a better understanding of the phenomenon of neck formation from the molecular point of view. We know from previous experience that the incipient point of instability for linear polyethylenes occurs about a factor of two in time earlier than the time for which the neck becomes visible. One of the continuum theories predicts that the incipient point of instability will occur when the instantaneous jump modulus goes to zero. If the model is valid, then it should be possible to devise tests for nondestructive evaluation.

### Stress-Cracking Test for ASTM

J. M. Crissman, L. J. Zapas, and G. M. Martin

This project concerns the development of an improved test method for the determination of the stress-crack resistance of ethylene plastics. Upon its completion, a description of the test method, as well as the appropriate statistical data will be submitted to ASTM Committee D-20.10 for their consideration. A preliminary report on the test method was presented to the ASTM Committee D-20.10 at their February meeting in San Diego, California. The test involves the use of a bent strip geometry, but differs from the current ASTM bent strip test in two important ways: the specimen is subjected to a constant applied stress and in the region of the bend, all specimens are maintained in the same geometry.

The failure time can be controlled to some extent by changing one or more of four parameters: the specimen thickness, the magnitude of the applied stress, the diameter of a metal cylinder (which determines the severity of the bend), and the temperature. In order to optimize these parameters, we are currently in the process of examining three different types of polyethylene which have widely different stress-crack behavior. Specimens of each polymer are being tested at two stress levels, two different cylinder radii, two different thicknesses, and at two or more temperatures. To determine the repeatability of the measurements, ten or more specimens are being tested for each set of parameters. Preliminary results indicate that two advantages of this test over the current ASTM bent strip test are improved repeatability and shortened testing time.

### Ductile and Brittle Behavior of Polyethylene

A. Peterlin

Creep experiments on isotropic linear polyethylenes by Crissman and Zapas have shown that failure occurs by brittle fracture at both very small and very large loads. At intermediate loads, the materials are ductile and after necking may deform to a very large draw ratio before they break at a substantially higher tensile stress.

The lifetime,  $t_b$ , at both very small and very large loads may be described as a sum of the microcrack nucleation time,  $t_n$ , and the microcrack growth time,  $t_g$ , in the brittle range and the shear band growth time,  $t_s$ , after which the sample necks and deforms drastically. It turns out that the nucleus of the microcrack formed under the tensile load may produce a craze perpendicular to the local stress and a shear band at about 45° to this stress. The craze growth time is an exponential function of the negative stress, while the shear band formation time is proportional to the inverse stress. If the curves representing the lifetimes of the two deformation modes as a function of the applied stress intersect, then the intersections separate the brittle from the ductile regime of the sample under tensile load. As a rule, with increasing temperature the shear band formation curve moves more rapidly to lower lifetimes than the microcrack growth curve. This expands the ductile region at the expense of the brittle region. A decreasing temperature acts in the opposite direction so that eventually the two curves do not intersect at all, and the material becomes brittle in the whole load region.



In this consideration, one has completely neglected the highest load range where the deformation is so rapid that the material becomes substantially heated by the deformation work, and hence, tends to fail like a liquid.

## Spectroscopic Investigation of Failure Mechanisms in Polyethylene

B. M. Fanconi, J. P. Colson, and K. L. DeVries<sup>1</sup>

The spectroscopic techniques of electron spin resonance and infrared spectroscopy are used to elucidate molecular mechanisms in polyethylene associated with exposure to  $\gamma$ -irradiation and with mechanical deformation and fracture. The irradiation studies, which have now been completed, not only gave information on the relationships between the number of new chemical species formed and the level of irradiation, but also provided a means of evaluating our experimental methods on samples in which the polymer molecules were not oriented during the exposure process.

Knowledge of molecular mechanisms associated with deformation and fracture in polymers is the main objective of the present work. Such information provides the basis for predicting long term performance from short time tests as well as insights into how the molecular composition may be changed to improve performance.

### Summary of Result on Irradiated Polyethylene

Measurements of the concentrations of free radicals by electron spin resonance and of new chemical species by Fourier transform infrared (FTIR) were carried out on polyethylene specimens exposed to  $\gamma$ -irradiation at dosages from three to fifty Mrads, both in the presence and absence of oxygen. The improved signal-to-noise capability of the FTIR method permitted a direct comparison of the free radical concentration and the resultant concentration of new chemical groups. It was found that approximately ten carbonyl groups and two carbon-carbon double bonds were formed per free radical. These results are comparable with previous estimates and form the basis for an investigation of chemical species formed during mechanical deformation and fracture.

### Chemical Changes Accompanying Mechanical Deformation and Fracture

The molecular mechanisms associated with mechanical deformation and fracture in polyethylene are elucidated through comparisons between FTIR spectra of undeformed and fractured specimens. Small variations in the concentrations of carbon-carbon double bonds, methyl groups, and carbonyl groups result from rupture of carbon-carbon backbone bonds and subsequent free radical reactions. These concentrations can be detected in difference spectra obtained through subtraction of the digital FTIR data. The ability to detect small concentration variations is enhanced by the superior sensitivity of the FTIR method over conventional dispersive infrared spectroscopy. The number and type of chemical groups formed are correlated with ESR measurements of the number of secondary radicals accompanying mechanical deformation and fracture.

Our results can be divided into two regimes associated with the rate of mechanical deformation. In one set of experiments, the polyethylene specimens in the shape of dumbbells were rapidly pulled in a tensile tester until ruptured, while in the other set specimens were allowed to deform under dead load conditions. In both cases, the deformed or fractured specimens were subsequently heated and pressed into thin sheets suitable for infrared analysis. In this manner, the difficulties inherent in comparing spectra of unoriented (undrawn) and oriented polyethylene which had plagued previous infrared studies of deformed and fractured polymers have been circumvented.

For the rapidly deformed specimens, we observed that the number of ketone groups decreases when compared to the reference polymer. This result is contrary to previous findings and suggests that bond rupture occurs preferentially near the ketone group and that subsequent

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<sup>1</sup>University of Utah.



reactions produce low molecular weight ketones which are volatilized during preparation of the specimens for infrared studies. Assuming that the ketone groups are preferentially located in the interlamellar regions, our findings support the notion that fracture occurs at lamellar interfaces.

When polyethylene specimens are slowly deformed, we observe the number of carbonyl and vinyl groups to increase, which is consistent with previously published reports. Experiments are in progress to substantiate these results on drawn polyethylenes to determine whether a relationship exists between the level of deformation and the concentration of each group.

### Fracture Mechanics of Polymers

E. Passaglia

In April of this year, a new project on the fracture mechanics of polymers was begun. A complete review of the literature, concentrating on the effects of plasticity and viscoelasticity, is well along. A review paper in these areas is contemplated.

Technical work has concerned itself with the viscoelastic nature of the craze material at the tip of a slowly moving crack. Published results by Ward and his co-workers [1,2,3] and by Weidmann and Döll [4] show that the shape of the crazed region is quite accurately represented by the Dugdale model [5], which was developed for plastic yielding in metals. In this model, the stress in the yielded zone (which corresponds to the crazed region) is a constant and equal to the yield stress, with the length of the zone increasing as the applied stress intensity factor is increased. In the polymer case, however, it has been shown [4] that the stress in the crazed region is proportional to the applied stress intensity, with the length of the crazed region remaining constant. Moreover, other experiments [6,7] indicate that the craze material is viscoelastic and not plastic. We, therefore, have the unusual result of a theory developed for an elastic-plastic material accounting well for observations on a viscoelastic material.

This can, in principle, be explained if the relaxation of stress in the craze in the growing crack is compensated for by the elongation provided as the crack grows, in just such a manner as to produce a constant stress within the craze. Since the shape of the craze region is known from these results, it is, in principle, possible to determine the relaxation function for the craze material. For the linear viscoelastic case (which is probably too simple for this situation), this determination involves calculating the Laplace transform of the crack displacement, calculating from this the Laplace transform of the relaxation function, and then inverting this transform. The last step is known to be a delicate mathematical operation, so that while mathematical difficulties have been encountered, preliminary results show that the method is feasible.

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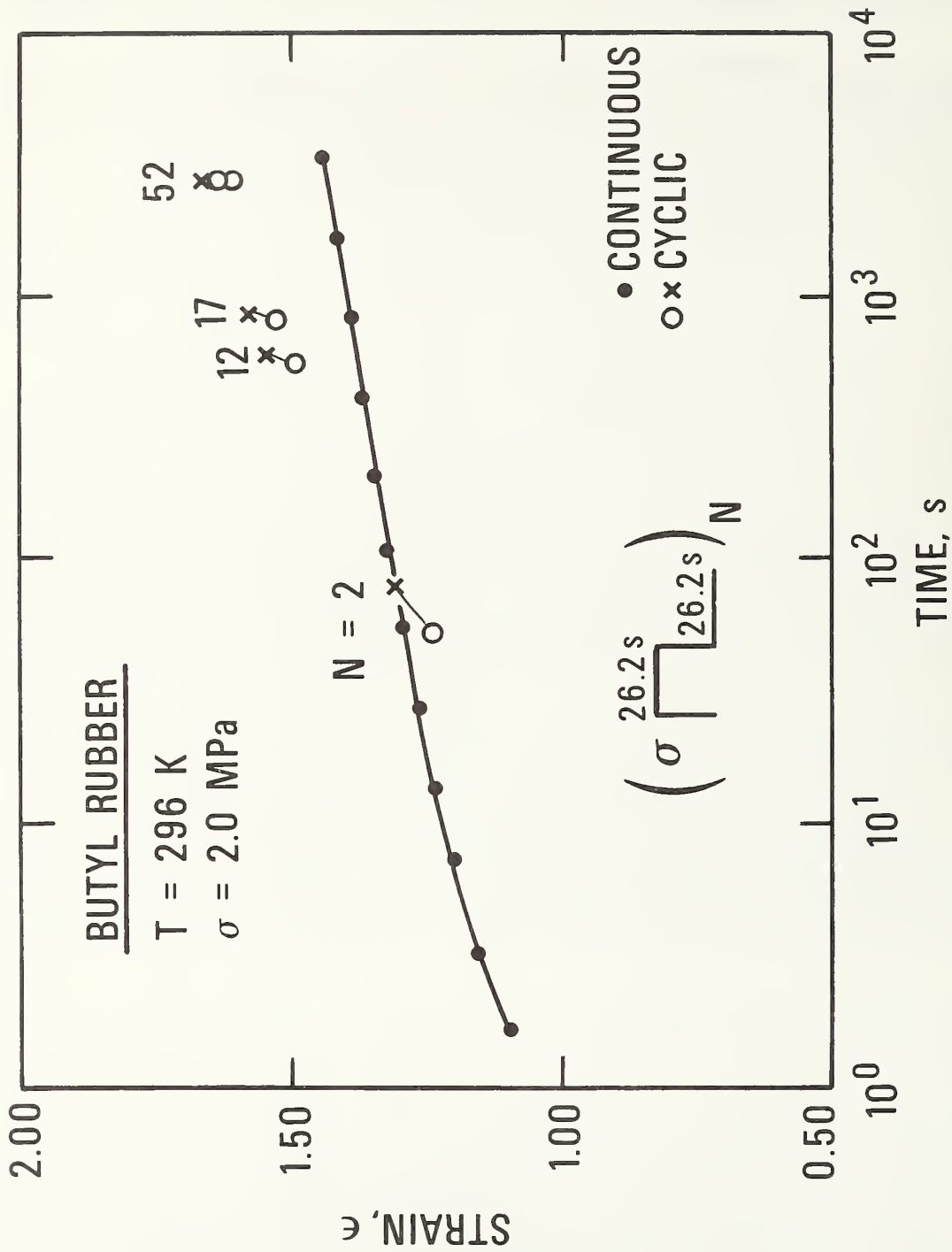


Fig. 1. Creep of carbon black filled butyl rubber under continuous (static) loading (●) and square wave zero-tension cyclic loading (○,x) at 2.0 MPa. (○) 1.6 sec. into step (x) 26.2 sec. into step.

R. W. Penn, G. B. McKenna, F. A. Khoury, and G. W. Bullman

This project is directed to the development of accelerated physical testing procedures and to the evaluation of candidate elastomers for use in circulatory assist devices. The project is supported by the National Heart, Lung, and Blood Institute of the National Institutes of Health under contract #Y01-HV-8-0003. Three candidate materials are under study along with a standard butyl rubber. The three candidate materials are a polyolefin rubber, a urethane-silicone copolymer, and a segmented polyurethane elastomer. During this year, all of these materials have become, or are becoming, available in adequate supply.

We have obtained results from both uniaxial and biaxial testing with both static and dynamic stress histories. Our results show that in static uniaxial loading the butyl rubber is superior to the polyolefin at short times (high stresses) but that this behavior reverses at long times (low stresses). Under dynamic (fatigue) loading, the failure times decrease with increasing test frequency but not rapidly enough to say that the samples fail after a constant number of cycles. Statistical analysis of the failure data shows that there is greater variability in the failure times for the polyolefin rubber than for the butyl rubber in all tests in which a comparison can be made.

Biaxial fatigue test results show that the urethane-silicone copolymer lasts longer than the polyolefin rubber, which lasts longer than the butyl rubber when they are compared at the same reduced pressures. For both the polyolefin rubber and the butyl rubber, the dependence of lifetime on stress is the same in static and fatigue loading. The butyl rubber in both cases shows a higher stress dependence. In the case of both rubbers, the variability in the failure times is greater in static testing than in dynamic testing. Data for the butyl rubber and preliminary results for the urethane silicone copolymer from biaxial fatigue tests at 23° and 37 °C reflect activation energies for the failure process of 22 kcal and 25 kcal, respectively.

Creep data under uniaxial loading have been obtained for all four elastomers. Creep rates range from 1.7 percent per decade of time for the segmented polyurethane elastomer to four percent per decade for the polyolefin rubber.

Examination of the urethane-silicone copolymer by optical microscopy shows heterogeneities on a coarser scale than has been previously reported. These structures consist of flattened spheroids with their short axes perpendicular to the plane of the sheet. Their sizes parallel to the plane of the sheet vary from a few micrometers up to about 30  $\mu\text{m}$ .

### Response of Carbon Black Filled Rubber to Cyclic Loading

G. B. McKenna and L. J. Zapas

We have been examining the deformation behavior of a carbon black filled butyl rubber in view of the BKZ constitutive equation. Failure behavior has been studied within the context of cyclic creep and a cycle shifted failure envelope.

For materials which follow BKZ type behavior, the single step stress relaxation response is a lower bound on the cyclic stress relaxation behavior, and the single step creep response is an upper bound on the deformations obtained in cyclic creep. In the responses observed for the carbon black filled rubber, we found that upon cycling the material, the creep and stress relaxation responses were outside these bounds. (See, for example, Figure 1). We also found that the softening was more emphatic in cyclic creep than in cyclic stress relaxation. Further work needs to be done in order to understand these results for materials which are nearly elastic in constant stress or strain histories. We have also found that the material creep response in constant load experiments is stiffer than that predicted from the BKZ constitutive equation. It is suggested that an adequate description of the material behavior might be obtained by developing a theory similar to the BKZ theory which includes competing effects of stiffening in creep and softening under load-unload cycling.

In studying the cyclic creep behavior of the butyl rubber, we found that the creep rate is dependent upon the waveform and frequency of the test. Also, unlike the case of static creep, the creep rate under the cyclic loading is a function of the stress level. An interesting point which arises in examining the cyclic creep data is that the square waveform load-unload cycle



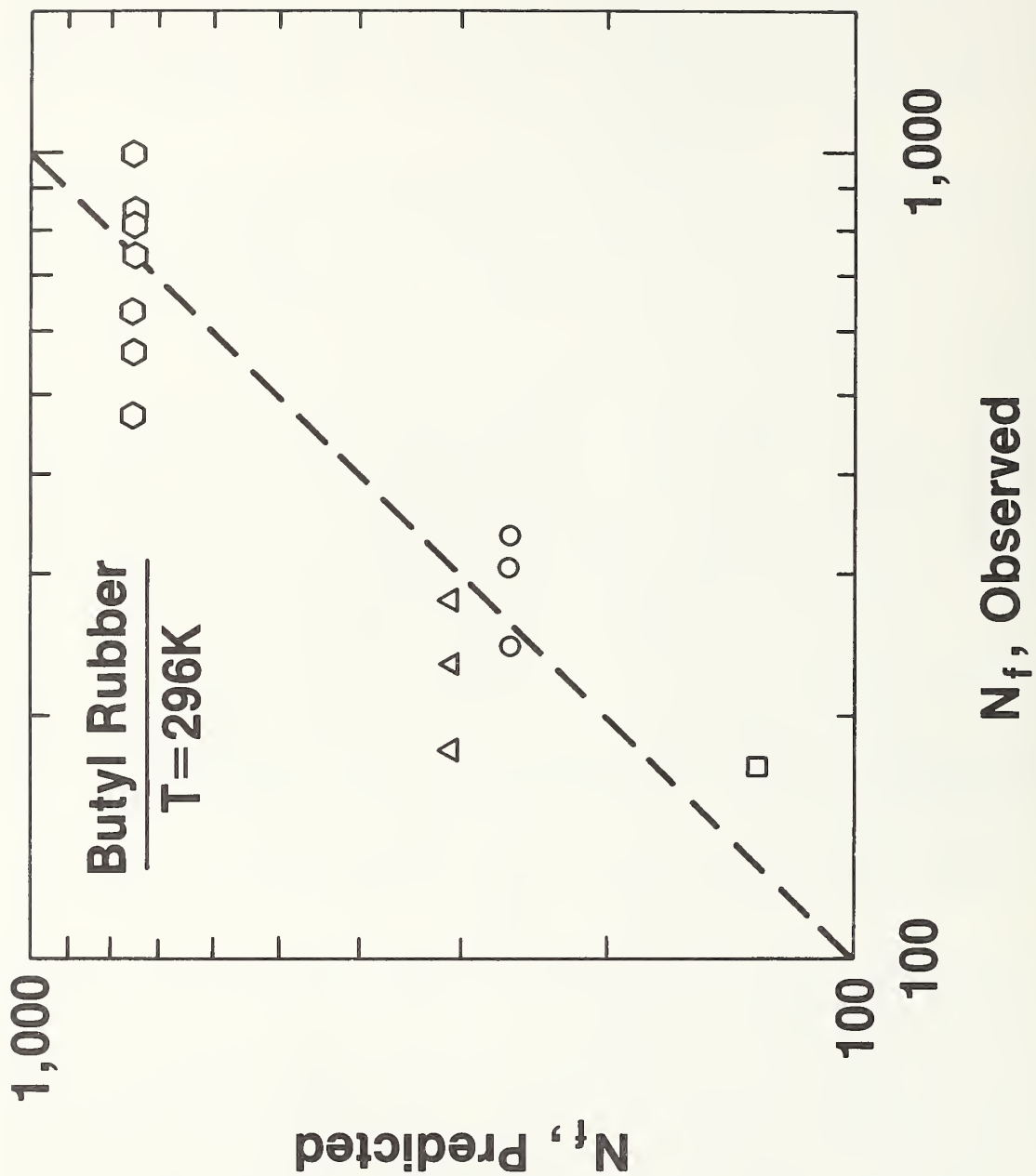


Fig. 2. Number of cycles to failure predicted using shifted failure envelope vs. observed number of cycles to failure for carbon black filled butyl rubber. Zero-tension fatigue with peak stress of 5.5 MPa. Loading: Sinusoidal (O) 0.002  $H_z$ ; (O) 0.01  $H_z$ ; ( $\square$ ) 0.09  $H_z$ . Square wave ( $\Delta$ ) 52.4 sec. cycles.

which had a test frequency of 0.02 Hz showed nearly the same behavior as the sinusoidal load-unload cycle at 0.01 Hz. This would indicate that stress softening occurs due to cycling but is independent of the rate of load application. The amount of stress softening depends upon both time and cycles. This can be seen from the fact that the amount of stress softening per cycle increases with decreasing frequency, and the stress softening per unit time increases with increasing frequency.

The lifetime of carbon black filled rubber in cyclic loading depends upon the test frequency and the waveform of the loading cycle (e.g., square wave vs. sine wave). We have been able to use cyclic creep data combined with the notion of a shifted failure envelope to account for the frequency and wave form dependence of the fatigue lifetime of carbon black filled butyl rubber.

In simple loading histories, failure of rubbers is readily described by a failure envelope for which the locus of stress at break vs. strain at break can be represented as a unique curve independent of stress history. In general, however, the failure envelope can be dependent upon the loading history. In addition, the amount of change may depend upon the stress. Since in our cyclic creep experiments we found that the amount of stress softening was relatively independent of waveform, and all of our tests were conducted at the same peak stress (5.5 MPa), we can express the change in the failure envelope due to cyclic loading by a shift factor  $a_{\sigma}$ . Then

$$\epsilon_{bc} = a_{\sigma} \epsilon_{bo} \quad (1)$$

where  $\epsilon_{bc}$  is the strain at break under cyclic loading,  $a_{\sigma}$  is a shift factor, which may depend on the level of stress, and  $\epsilon_{bo}$  is the failure strain (at the same stress) in a simple deformation history (i.e., creep, stress relaxation, constant rate of deformation). With this assumption, the same shift factor should permit prediction of all of our cyclic failure data by extrapolation of the cyclic creep strain data to the  $\epsilon_{bc}$  determined from Eq. (1) and one set of the failure data. The results are shown in Figure 2 in a plot of the predicted number of cycles to failure vs. the observed number of cycles to failure. The points show the data, and their distance from the dashed line gives the deviation from the predictions. Given the limited number of data, the agreement is good. The observed deviations could arise from variability in the cyclic creep data, a possible history dependence (which we have ignored) of the amount which the failure envelope shifts, as well as the normal amount of variability in the number of cycles to failure in fatigue type testing.

Work is continuing in our study of the effects of cyclic loading on creep and failure of carbon black filled rubbers. An effort is being made to find an appropriate constitutive law to include the effects of stiffening in creep and softening due to cycling of these materials. Experiments are being conducted to assist in this development. Experimental work is also continuing to explore in more detail the applicability of the cycle shifted failure envelope to the description of fatigue lifetime of filled rubbers.

#### Relationship Between Morphology and Mechanical Properties of Ultra High Molecular Weight Polyethylene

G. B. McKenna, F. A. Khoury, and J. M. Crissman

The starting material used in the manufacture of the polymeric components of orthopedic prostheses is ultra high molecular weight polyethylene (UHMWPE) in its nascent state (i.e., as polymerized). The devices made from UHMWPE are fabricated in one of two ways: a) they are machined from rods or blocks prepared from the raw polymer (usually by compression molding) or b) they are molded directly from the nascent polymer powder into the desired shape. In clinical use, the long term performance of implants made from UHMWPE is determined by time dependent phenomena such as creep, fatigue, and wear. The manner in which these phenomena depend upon the thermal history and resultant morphology is not well understood.

Under contract with the FDA Bureau of Medical Devices, we are studying the relationship between morphology and the mechanical properties of UHMWPE. Our work has three specific goals:

- (1) To determine the influence of polymer morphology on the time dependent mechanical properties of UHMWPE and to identify thereby the fine structural parameters which significantly affect long term performance.
- (2) To generate data in the areas of compressive creep, stress relaxation, and time dependent failure behavior which will be useful as a basis for evaluating the future and current devices made from UHMWPE.
- (3) To devise measurement techniques which will be relevant to the development of standard test methods for characterizing the time dependent mechanical properties of implants fabricated from UHMWPE.

During this first year of the project, we have focused our efforts in three areas: a) developing the molding capabilities and techniques to fabricate samples of UHMWPE in a reproducible manner; b) characterization of the morphology of the UHMWPE polymer as received after molding and after deformation and failure; and c) characterization of the time dependent mechanical behavior of UHMWPE.

We have developed a technique for fabricating sheets of UHMWPE using a vacuum mold. These sheets are used for uniaxial and equibiaxial test specimens. We are currently developing a technique for fabricating cylindrical specimens for compression testing.

Morphological characteristics of the UHMWPE raw polymer and of the fabricated sheets are being characterized using scanning electron microscopy, wide, and small angle x-ray diffraction, optical microscopy, and differential scanning calorimetry. Initial work has shown that the raw polymer has a grain-like structure which is carried over into the molded sheets. Also, the melting point of the raw polymer is significantly higher than that of the molded sheets, which indicates a higher degree of crystallinity in the raw polymer. X-ray diffraction patterns from samples which have been drawn to failure and then released show that there is considerable permanent orientation. Small angle x-ray diffraction shows changes occurring in the lamellar texture due to the deformation process.

The uniaxial creep and failure behavior of the UHMWPE is being characterized. Room temperature testing gives the interesting result that UHMWPE does not neck, but rather deforms and draws homogeneously to failure. This is unlike the behavior of lower molecular weight polyethylene. Our test results to date indicate that the time to failure in uniaxial testing is shorter for continuous loading than it is for zero-tension cyclic (fatigue) loading at 0.002 Hz. Further testing needs to be performed to substantiate this result and to determine effects of test frequency on lifetime.

### The Crystallization, Morphology, Deformation, and Orientation of Polymers

F. A. Khoury and L. H. Bolz

Investigations of the morphology of crystalline polymers during the past year have been mainly in the two areas outlined below.

#### The Habits of Polyethylene Crystals Grown From Solution at High Temperatures

The objective of this investigation is to determine the effects of crystallization temperature, molecular weight, and polymer concentration on the morphology of chain-folded polyethylene crystals grown from solution at temperatures which approach and overlap the temperature range ( $\sim 118-130$  °C) in which the polymer crystallizes isothermally in the form of axialites or spherulites upon cooling from the molten state.

In an earlier experimental study, polyethylene fractions (molecular weights 11,400-100,500) and unfractionated ultra high molecular weight polyethylene (molecular weight  $\sim 4.5 \times 10^6$ ) were crystallized from 0.01 percent solutions in various solvents in the temperature range 95-115 °C. Distinct trends in the effects of molecular weight and undercooling on the lateral growth habits of the crystals were observed. During the past year we have attempted to grow crystals from solutions of the same polymer concentration (0.01 percent) at even higher temperatures. This has been achieved with a fraction of molecular weight 28,900, crystals of which were grown at temperatures up to 120 °C using docexanol as a solvent.



In an attempt to deduce the nature of the conformation (e.g., tent-like or variously curved) of the various species of polyethylene crystals we have grown between 95° and 120 °C, a study is under way in which scanning transmission electron microscopy and small-area (diameter ~0.4 μm) electron diffraction are being used to determine the details of the inclination of the chain stems relative to the surface of the lamellae. Of particular interest in this connection are crystals which, earlier results indicated, have asymmetric (apparently S-like) cross-sectional shapes when viewed along the b-axis direction. Our present aim is to determine how widespread and varied is the manifestation of this feature among the various types of polyethylene crystals we have grown. We believe that such crystals will serve as useful models for the constituent twisted lamellae in polyethylene spherulites grown from the melt at high undercoolings. It has recently been reported in the literature that the constituent lamellae in such spherulites, which lamellae are oriented with their b-axis parallel to the spherulite radius, exhibit S-shaped cross-sections when viewed along that direction [R. H. Olley, A. M. Hodge, and D. C. Bassett, J. Poly. Sci., Poly. Phys. Ed., 17, 627 (1979)].

### The Morphology of Compression Molded Ultra High Molecular Weight Polyethylene

Aspects of the morphology of compression molded ultra high molecular weight polyethylene (UHMWPE, molecular weight ~4.5 x 10<sup>6</sup>), and the fine structural changes induced in molded sheets of this material as a result of uniaxial deformation have been examined. This work is part of a new project which is sponsored by the FDA, and whose objectives are to characterize the mechanical properties of UHMWPE (G. B. McKenna and J. M. Crissman) and to examine the relationships between these properties and the morphology of the polymer. These relationships, which bear importantly on the durability of products made from UHMWPE, are of particular interest to the FDA because numerous components of artificial orthopedic implants (e.g., hip cups, tibial plateaux) are made from this polymer.

Sheets of UHMWPE which were compression molded at temperatures in the range 190-230 °C and were subsequently cooled slowly to room temperature, all exhibited a memory of the grain-like character of the as-polymerized raw polymer powder which is the usual starting material from which the implant components are manufactured. The density of the sheets was 0.936. Examination under the optical microscope, with cross polarizers, of thin cross-sections cut from the sheets revealed a heterogeneous distribution of birefringent structures of varying sizes. In some regions the sections had a very fine granular appearance. In others, larger structures were seen, the largest of which were distinctly spherulitic. Small angle x-ray diffraction patterns obtained from the sheets did not exhibit any distinguishable diffraction ring. This is either because the thickness of the lamellae was greater than the largest spacing (~300Å), which can be resolved in the present instrument, or because there is a large distribution in the thickness of the lamellae due to the fact that the polymer was not crystallized isothermally.

Dumbbell shaped samples cut from sheets molded at 200 °C were subjected to uniaxial extension at 1 mm/min at 23 °C, 37 °C, and 70 °C. In contrast with lower molecular weight linear polyethylene (e.g., molecular weight < 200,000) the samples deformed uniformly and did not exhibit any necking even up to the breaking point. Current experiments are aimed at determining the recovery of samples from deformation at 23 °C, 37 °C, and 70 °C to various strains below the breaking strain. Low angle and wide angle x-ray diffraction and scanning electron microscopy are being used in an attempt to determine the nature of the permanent and recoverable changes in orientation and fine structure resulting from deformation to various strain levels. Structural changes resulting from stress relaxation will also be examined.

### Polymeric Sealants for Geothermal Energy

E. A. Kearsley

The Department of Energy envisions that within a matter of decades the exploitation of geothermal energy resources will be making a substantial contribution to our national energy needs. However, in order for this to be accomplished, it is necessary to stimulate several associated technologies. The Division of Geothermal Energy of DOE has accordingly requested help in developing tests of polymeric materials to screen likely candidates for use as geothermal sealants. Since there are many forms of seals used in the drilling and production of geothermal wells, and down-hole environments vary considerably among the different well locations, it is not possible to specify reasonable requirements for geothermal sealants in general. The most interesting and energetically important wells are potentially those with

ambient down-hole temperatures greater than 260 °C and with strongly corrosive reducing (rather than oxidizing) atmospheres. The sealant materials should perform (frequently this means maintaining large elastic stresses for fixed deformations) under these demanding conditions for time periods ranging from hours for well-drilling sealants to months or years for production seals. Current technology for such seals is largely based on developments for the petroleum industry and is, consequently, adapted to lower temperatures and less corrosive conditions.

At present, various ad hoc lifetime tests are used by designers of geothermal equipment to test specific seals under conditions simulating the intended use. Such tests are very specialized and inconvenient. Failures of the seals are observed to occur either because the sealant hardens and eventually cracks or because the sealant softens and flows. The program on geothermal sealants in the Polymer Science and Standards Division aims at a more fundamental test which gets at the causes of this behavior so that the results can be used to design seals for whatever configuration or geothermal environment is needed. This is to be achieved by measuring the rates of formation and of breaking of bonds (cross-links or equivalent) affecting the elastic properties of sealant materials aging under controlled conditions. With information on how these rates depend on the parameters of the down-hole atmosphere, it should be possible to estimate accurately the long-time behavior of seals of any geometry (e.g., packer seals, o-rings, chevron seals, etc.) in any conditions of interest.

The customary way of measuring rates of cross-link breaking and forming is that developed by Tobolsky et al. to study oxidative degradation of rubber. In that method, two sets of measurements are required: 1) the stress relaxation of material aging while deformed and 2) the change in elastic modulus of material aging in an undeformed configuration. The latter data can be collected rather routinely, but stress relaxation is an inconvenient experiment, particularly under conditions corresponding to geothermal down-well atmospheres. Consequently, we have worked out the theory of a method to substitute permanent-set data for the stress relaxation data needed for the Tobolsky method. The theoretical work for this is completed, but there remains the task of establishing the most practical experimental methods of making the measurements.

Currently, the technique is being evaluated using simulating temperatures but not simulated geothermal fluids. The test samples are sealed in evacuated glass tubes during aging (at 260 °C) to avoid oxidation, since geothermal atmospheres are normally reducing rather than oxidizing. The conditions necessary to simulate complete relaxation prior to the measurement of permanent-set are still not completely known. Concurrently, an apparatus is being constructed to age samples in more realistic conditions, that is, in water compressed up to pressure of 5000 psi at temperatures up to 350 °C. Such conditions may induce hydrolysis of the sealant materials, thus affecting bond stability.

### Characterization of Polymeric Solids by $^{13}\text{C}$ NMR

D. L. VanderHart and S. J. Kryder

High resolution  $^{13}\text{C}$  NMR of solid samples has been greatly aided by the recent development of magic angle sample spinning (MASS) together with the technique of high-power proton decoupling. With MASS,  $^{13}\text{C}$  NMR lines in solids appear at their isotropic chemical shift positions, just as they do in liquids, thereby enabling one to separate resonances corresponding to chemically different carbons. In the absence of MASS,  $^{13}\text{C}$  lineshapes are much broader, and different  $^{13}\text{C}$  resonances are likely to show a modest to severe overlap. Nevertheless, these lineshapes in chemically simple materials, e.g., polyethylene (PE), contain interesting orientational information, and as discussed below, we have made use of such measurements to follow the orientational behavior of noncrystalline PE chains during annealing. For the last two years MASS capability has also been available on a spectrometer with a magnetic field of 1.4T. This past year, however, a 4.7T superconducting-solenoid spectrometer was installed as an NML facility. This spectrometer, although principally equipped for liquid-state NMR, also has MASS capability in conjunction with  $^{13}\text{C}$  NMR in solids, and this facility is expected to become a more significant instrument for our program because of its higher sensitivity.

#### Studies of Orientation in the Non-Crystalline Regions of Drawn Polymers

It has been demonstrated here that it is possible to separate  $^{13}\text{C}$  signals in polyethylene (PE) arising from chains having preferentially high mobility relative to crystalline chains.



Furthermore, it is possible to analyze the distribution of orientations. These studies are being extended to include ultra high molecular weight drawn PE whose macroscopic drawing characteristics (maximum draw ratio, lack of necking) are quite distinct from the lower molecular weight samples. Further, if samples can be obtained, it would be of interest to examine Pennings-type solution-shear-aligned PE fibers because the morphology is established by crystallization in shear flow rather than by deformation. Thus, one might expect more extended chain material but perhaps a reduction of entanglement-related connectivity. There is current effort to extend this method for measuring non-crystalline orientation to polyethylene terephthalate (PET), which is a commonly used commercial fiber. In PET, preliminary experiments have shown promise that the CH<sub>2</sub> resonance can be used to determine orientation in the non-crystalline region. But PET is more complicated than PE in that the ratio of relaxation times (molecular mobilities) between the crystalline and non-crystalline phases is expected to be smaller than in PE; furthermore, there is some argument about whether crystallinity means organized molecular packing or merely all-trans chains. Further work on these substances will also involve correlations with mechanical properties as well as the acquisition of a non-spinning probe for the 4.7T NML spectrometer to take advantage of its higher sensitivity. Use of non-spinning <sup>13</sup>C NMR as a comparative tool in monitoring orientation in glassy polymers below T<sub>g</sub> should also be investigated.

### Resolution in <sup>13</sup>C MASS Spectra in Polymers

This work is aimed at evaluating the capabilities of the <sup>13</sup>C MASS technique for 1) studying relaxation of individual carbon sites, 2) studying tacticity and/or conformation in the solid state, 3) using the method as an analytical tool, and 4) using linewidths as a source of information about molecular motion or molecular packing.

We are currently in the final stages of preparing an extensive manuscript on the subject of resolution in the <sup>13</sup>C NMR of hydrocarbons using MASS. One result of this study is that molecular motion in the mid-kilohertz region produces overwhelming broadening for protonated carbon resonances. Thus, if one wishes to perform analytical measurements on a sample and needs best-available resolution, the ability to vary temperature and move to a region where motions do not create inordinate broadening is highly desirable. Another outgrowth of looking into the resolution question is the recognition that solid polymers often exhibit chemical shift dispersions and discrete magnetic inequivalencies which are unique to the solid and which are averaged in solution. Chemical shift dispersions can arise from variation in the packing of chains. This is a difficult problem to address theoretically because of the complex nature of the chemical shift expressions. This problem was addressed experimentally by looking at changes in resonance positions of the interior methylene resonances in the alkanes as a function of crystal structure. The n-alkanes are found to have four crystal habits, and corresponding resonances were found to range over 1.3 ppm. Thus, it was concluded that packing variations, particularly in glassy polymers, can account for chemical shift dispersions of the order of 1-2 ppm and that no conformational variations need be invoked to explain such dispersions. This is an important perspective to have gained.

With respect to discrete magnetic inequivalencies, consider crystalline isotactic polystyrene which shows six distinct aromatic carbon resonances, whereas only four are observed in solution. Variable temperature studies of the collapse of such inequivalencies in the solid would give very specific information about the frequency and nature of molecular motion, e.g., initial collapse from six to four resonances in polystyrene would correspond to rotation of the ring about the aromatic-aliphatic C-C bond direction at a frequency closely related to the splitting. Therefore, one of the badly needed instrumental modifications required is to design and build a variable-temperature MASS probe. It is not a simple matter to design such a probe without sacrificing sensitivity. Nevertheless, it is a high priority item to equip both the high and low field instruments with such a probe in order to:

- (1) move away from undesirable temperatures to get improved resolution,
- (2) study temperature dependent motions in polymers,
- (3) improve quantitation (will be discussed) for analytical applications, and
- (4) study conformational equilibria.



## Quantitation in $^{13}\text{C}$ NMR Spectra of Solids

If a broad-band pulse is applied to  $^{13}\text{C}$  spins having equilibrium Boltzmann populations, resulting NMR spectra are quantitative in the sense that each  $^{13}\text{C}$  nucleus appears to make an equal contribution to the total signal. Because  $^{13}\text{C}$  signals are inherently weak and because many carbons have no directly bonded protons (thereby making their relaxation times long), the method just described is seldom used to generate  $^{13}\text{C}$  signals. Rather, cross-polarization techniques are usually used in which  $^{13}\text{C}$  magnetization is transferred from protons to carbons. While this method generally enhances the  $^{13}\text{C}$  signals over the first experiment by a factor of 3-4, and further, allows one to repeat scans in a time determined by the proton rather than slowest carbon relaxation, the quantitateness of the resulting spectra is no longer assured. On theoretical grounds, distortions of true intensities can be expected both when molecular motions are in the mid-kilohertz range and when molecules are isotropically tumbling and translating. This general area deserves more attention in polymers, particularly in blends, copolymers, or multiphase polymers. Such distortions are observed in the spectra of PE, as well as polycarbonate and polyethylene oxide. For exploring the problem of quantitation, temperature is an essential variable. A particular area where quantitation problems are likely to be severe is analysis of extent of curing, e.g., in dental composites.

### Impact and Use of the High Field NMR

There is no doubt that sensitivity per scan is higher at high field, but relaxation times for slowly moving molecules may increase tenfold with respect to the lower field, thereby making relative sensitivities comparable. A perspective must be developed. Resolution using MASS at high versus low field is still an open question. It is only a rare case where resolution dramatically improves; nevertheless, a more complete perspective must be developed here in order to optimize spectral information.

### Acoustic Emission of Crazing Polymers

A. Peterlin, R. E. Green<sup>1</sup>, B. B. Djordjevic<sup>1</sup>, and R. C. Murphy<sup>1</sup>

After repeated attempts to observe acoustic emission in strained poly(methyl methacrylate) (PMMA), we have concluded that the emission occurs in the millisecond range where the noise background of the stretching machine completely masks the acoustic emission. Therefore, a statically bent PMMA specimen was observed with a reflected laser beam during the wetting of the bent surface by a droplet of benzene. The formation of crazes and vertical displacements of the surface of the bent slab of PMMA were observed. Indeed, the duration of the pulse, detected by the vertical motion of the polymer surfaces reflecting the laser beam, turned out to be in the millisecond range. Time extension of the pulse has shown a fine structure which is mainly caused by the interference of the primary signal with the waves reflected at the fixed ends of the bent slab. The reflections distort the acoustic emission signal to such an extent that its time dependence cannot be determined.

The optical method has definitively shown that the craze forms relatively slowly in about 1 ms and that it forms in a great many single steps of almost equal amplitude. Concurrently, the bent slab assumes a more bent position as a consequence of the elongation of the convex bent surface by the newly formed craze. Since the new position is obtained by damped oscillations which displace the reflecting surface of the bent slab vertically, the laser signal also records this movement which has no direct connection to the acoustic emission of the craze.

### Non-Linear Elastic Behavior of Polymeric Materials

E. A. Kearsley, G. B. McKenna, and L. J. Zapas

The theory of finite deformations of an elastic medium is often used with the added restriction of incompressibility of the medium. This restriction makes possible the solution of several classes of problems in terms of an unspecified strain-energy potential; however, it excludes the possibility that the elastic material properties depend on pressure. To make possible the use of these solutions in cases where material properties are pressure dependent,

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we have derived a different form of the theory. Through a Legendre transformation, the equations of finite elasticity of a compressible medium were formulated in terms of an elastic potential whose independent variables are pressure and shear rather than the usual deformation invariants. This elastic potential has no explicit dependence on volume change. Rather, the two derivatives of the potential are equal to the stress deviator and the volume change. The form of the resulting elasticity equations makes clear the mechanical effects of introducing a large ratio of bulk modulus to shear modulus into elasticity theory and leads to a theory of an (almost) incompressible medium for which the shear modulus depends upon the isotropic part of the stress. Through the elastic potential, some specific relations among the pressure coefficients of the mechanical moduli and the change of volume with deformation can be derived. These relations are accessible to experiment, and they suggest an interesting method of elucidating the effects of pressure on the mechanical behavior of natural rubber.

Our recent work with the theory of rubber elasticity has shown that the strain-energy function for elastomers (which determines the non-linear elastic behavior) may be measurable from experiments simpler than hitherto thought possible. However, the method depends upon the strain-energy relation having a special form (the Valanis-Landel form). Although some data already in the literature support this requirement, there are also some published data which raise questions about its validity. The point needs clarification. Experiments are under way to test the validity of the Valanis-Landel form through an experiment on simultaneous extension and torsion of cylinders of elastomers.

### Non-Linear Viscoelastic Behavior of Poly(methyl methacrylate)

G. B. McKenna and L. J. Zapas

We have conducted single step stress relaxation experiments on cylinders of poly(methyl methacrylate) (PMMA) where we measured torque and normal force responses as functions of time and angle of twist. By assuming that torsion is an isochoric motion and that volume effects are separable, we obtained [1] isochronal values for the derivatives of the strain potential function,  $\partial W/\partial I_1$  and  $\partial W/\partial I_2$ . Our results showed that  $\partial W/\partial I_1$  is negative, while  $\partial W/\partial I_2$  is positive and greater in magnitude than  $\partial W/\partial I_1$ . These findings provided the possibility of explaining the phenomenon observed by Sternstein and Ho [2] that the single step stress relaxation responses of PMMA are different in torsion and in simple extension. Specifically, the time rate of decay of stress is significantly higher in torsion than in extension. This phenomenon was observed at small strains where the stress responses in torsion and extension were linear in the appropriate strain measures.

Using a form of the viscoelastic strain potential function similar to the Valanis-Landel [3] form of the strain energy function for elastic materials, we calculated the response in simple extension from our torsion-normal force determined values of  $\partial W/\partial I_1$  and  $\partial W/\partial I_2$ . Although we obtained good agreement between our calculated and our observed extensional behaviors, we could not account fully for the observations of Sternstein and Ho [2].

Table 1 shows some isochronal data for  $\partial W/\partial I_1(t) = W_1(t)$  and  $\partial W/\partial I_2(t) = W_2(t)$  for measurements made on PMMA in the form of both annealed rod and unconditioned tube. We remark on three things about these data. First,  $W_1(t)$  is negative while  $W_2(t)$  is positive and of greater magnitude than  $W_1(t)$ . This is different from the behavior usually observed in rubbers and polymer melts, where  $W_1$  is usually positive and larger than  $W_2$ . Another observation we can make is that  $W_1(t)$  and  $W_2(t)$  exhibit different time dependences.

Also, the time dependence of the modulus,  $2(W_1+W_2)$ , is different from that of either  $W_1(t)$  or  $W_2(t)$ . (At the limit of small strains, i.e., in the linear range, the modulus  $G(t) = 2[W_1(t) + W_2(t)]$ ). Finally, the magnitude of  $W_1(t) + W_2(t)$  is different for the two different PMMA's. This is not attributable to the geometry difference but may be due to the differences in both source and thermal histories of the materials.

Table 1

Some Isochronal Values of  $W_1(t) + W_2(t)$ ,  $W_1(t)$  and  $W_2(t)$  for PMMA

Annealed Rod								
	$W_1+W_2$		$W_1$	$W_2$		$W_1+W_2$	$W_1$	$W_2$
	$\Psi R$	GPa	GPa	GPa		GPa	GPa	GPa
<u>1.64s</u>	0.00252	0.63	-2.19	2.82	<u>1678s</u>	0.488	-1.94	2.43
	0.00946	0.59	-1.98	2.57		0.456	-1.39	1.84
	0.0126	0.58	-1.82	2.40		0.442	-1.15	1.60
	0.0252	0.53	-1.10	1.63		0.379	-0.616	0.995
Unconditioned Tube								
<u>1.64s</u>	0.0095	0.48	-1.24	1.72	<u>1678s</u>	0.36	-0.79	1.15
	0.012	0.46	-1.24	1.70		0.35	-0.76	1.11
	0.016	0.45	-1.14	1.59		0.33	-0.65	0.98
	0.0208	0.44	-0.96	1.40		0.31	-0.47	0.78

From these data we determined isochrones for the viscoelastic V-L function  $w'(\lambda)$  for both the rods and tubes. From the  $w'(\lambda, t)$  we then calculated  $\sigma_{11}(t) - \sigma_{22}(t)$  for simple extension. The agreement between the calculations and the experiments was within the uncertainty for our values of  $w'(\lambda, t)$ . (This uncertainty in the small strain region is approximately  $\pm 15$  percent due to the large uncertainties in the normal stress measurements in this region). Of greater interest is the comparison of the relaxation rates in extension and torsion.

Table 2 summarizes our results and those of Sternstein and Ho [2]. The relaxation rates given in Table 2 are calculated from the slopes of log (stress) vs. log (time) plots. There are several things about these data which need to be discussed. First, Sternstein and Ho obtain greatly different rates of relaxation in extension and torsion (-0.0195 vs. -0.0329) at strains of  $\epsilon = 0.005$  and  $\gamma = 0.01$ , respectively. Our data in torsion show a slightly higher relaxation rate than theirs for  $\gamma = 0.01$  which increases as  $\gamma$  increases. Also, our data indicate that there is little difference in relaxation rates in extension and torsion at strains less than  $\epsilon = 0.02$  and  $\gamma = 0.04$ . But at strains of  $\epsilon = 0.02$  and  $\gamma = 0.04$  and higher, we find that there is a more rapid torsional relaxation rate than extensional relaxation rate (-0.058 vs. -0.047). We are currently planning experiments to further elucidate these differences and perhaps account for the differences between our data and those of Sternstein and Ho.

Table 2

Relaxation Rates for PMMA for Different States of Deformation

Strain	Relaxation Rate <sup>1</sup>			
	Tension Predicted	Observed	Torsion <sup>2</sup>	Simple Shear <sup>3</sup>
<u>Data of Sternstein &amp; Ho<sup>1</sup>:</u>				
$\epsilon = 0.005; \gamma = 0.01$	--	-0.0195	-0.0329	--
<u>Unconditioned Tubes:</u>				
$\epsilon = 0.01; \gamma = 0.02$	-0.0397	-0.0384	-0.0377	-0.0450
$\epsilon = 0.02; \gamma = 0.04$	-0.051	-0.047	-0.0581	-0.0634
<u>Annealed Rods:</u>				
$\epsilon = 0.005; \gamma = 0.01$	-0.0370	-0.0319	-0.0345	-0.0395
$\epsilon = 0.0075; \gamma = 0.015$	-0.0371	-0.0335	-0.0360	-0.0420

<sup>1</sup>Calculated from the slope of log (stress) vs. log (strain) plots.  
Rate is per decade of time.

<sup>2</sup>Observed experimentally.  $\gamma$  is the maximum strain in the tube or rod.

<sup>3</sup>Calculated from values of  $W_1$  and  $W_2$  obtained from torsion-normal force measurements.  $\gamma$  is the shear strain.



## References:

- (1) G. B. McKenna and L. J. Zapas, "Determination of the Time Dependent Strain Potential Function in Poly(methyl methacrylate)," paper presented at the 49th Annual Meeting of the Society of Rheology, Houston, Texas, October 1978.
- (2) S. S. Sternstein and T. C. Ho, "Biaxial Stress Relaxation in Glassy Polymers: Poly(methyl methacrylate)," J. Appl. Phys., 43, 4370 (1972).
- (3) K. C. Valanis and R. F. Landel, "The Strain Energy Function of a Hyperelastic Material in Terms of Extension Ratios," J. Appl. Phys., 38, 2997 (1967).

### Retractive Forces in Drawn Low Density Polyethylene During Annealing

A. Peterlin, R. Russo<sup>1</sup>, F. DeCandia<sup>1</sup>, and V. Vittoria<sup>1</sup>

The retractive forces in drawn low density polyethylene depend on temperature and time. At room temperature, the material looks fairly stable. Above 70 °C, the drawn sample starts to shrink. The shrinkage forces can be observed on a material with fixed ends. At a given temperature, they first increase to a maximum and then drop to a relatively high limiting value. The maximum force and the asymptotic value have a maximum at about 90 °C.

If the sample is heated at a sufficiently slow rate, the restoring force reaches a maximum at about 90 °C and subsequently drops almost to zero near the melting point of the material. The molecular explanation of the observed effects is based on the mobilization of taut tie molecules and on their relaxation at the high temperature of the annealing which permits a pulling of chain sections from the crystal blocks in which the taut tie molecules are fixed. During cooling, the restoring forces are substantially lower than during heating as a consequence of the relaxation of the taut tie molecules by the annealing effect of the previous heating.

### Permeation Performance of Polyethylene Used in Containers for Hazardous Materials Transportation

J. C. Phillips

The initial phase of this work involved the development of test methods for the permeation performance of polyethylene shipping containers to be used by the Department of Transportation. These experiments consisted of weight loss determinations for an n-alkane series, n-alcohol series, and n-carboxylic ester series. The loss rate,  $\dot{Q}_A$ , results were correlated with an effective carbon atom number,  $n_e$ , for each compound. Due to limited chain lengths ( $N_A \leq 8$ ), the shorter members of the alcohol and ester series showed deviations from linear behavior of  $\log \dot{Q}_A$  versus  $N_A$ .

The final phase of this work was concerned with loss rate measurements at  $t = 50$  °C for permeants of the n-alcohol and n-carboxylic ester series in which chain lengths were extended to  $N_A = 16$ . For the permeants studied and the polyethylene (PE) bottles used ( $\rho \sim 0.92$  g/cm<sup>3</sup> and  $\rho \sim 0.94$  g/cm<sup>3</sup>), the effective carbon atom number was reasonably correlated with the loss rate (i.e.,  $\log \dot{Q}_A$  versus  $n_e$  was linear and parallel for each density bottle). By using loss rate measurements from the low density bottle for a group of miscellaneous compounds (1,2-dichloroethane, acetone, methyl ethyl ketone, acetonitrile), the loss rate for the high density bottle was adequately predicted for these compounds.

This study has verified, at least for the permeants and PE bottles used, that the effective carbon atom number is a convenient parameter for transferring the results of permeation measurements among shipping containers made from various PE resins and, thereby, simplifies the prediction of transmission performance.

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## Durability of Paper

J. C. Smith, E. E. Toth, and E. L. Graminski

Paper used to make currency should have a good balance between durability and cost, as the replacement of worn out currency is an expensive operation. Because of this, the Bureau of Engraving and Printing supports work at NBS to identify and characterize those aspects of the morphology of paper networks which affect durability. The research results are expected to contribute to the development of durable paper made from blended wood pulps instead of the more expensive cotton and linen pulps presently used.

To achieve these objectives, it is necessary to have an improved understanding of the relationship between the structure of paper, the morphology of the fibers, the processing conditions, and the mechanical and physical properties of the paper and its components. Over the past several years, studies at the National Bureau of Standards on the bondability of the pulp fibers and on the cellulose-water interaction in rag and wood pulps have helped to provide some of this background information.

Parameters for characterizing interfiber bond strength can be obtained from tensile tests on a low density open-web handsheet prepared from the pulp to be evaluated. The force-elongation curve from a specimen of this handsheet contains numerous force drops, each drop caused by the breakage of a bond between fibers constituting the handsheet network. The relative number of bonds per unit area can be characterized by the average elongation between bond breaks. The bond strength can be characterized by an average of the force-drop magnitudes, or by an average of the energy losses resulting from the force drops. The average of the force levels obtained in a series of tests can also be used to characterize bond strength. The above parameters, however, are not very precise because of fluctuations in the uniformity of the test specimens.

Recent work has shown that the force elongation curve of a low density open-web test specimen has the form

$$F = A[\exp(x/x_c) - 1],$$

where  $F$  is the force, and  $x$  is the elongation. The two parameters,  $A$  and  $x_c$ , are sensitive to the number of fibers per unit area in the specimen tested. Moreover, during a test,  $A$  and  $x_c$  vary in value as the test proceeds, reflecting damage to the specimen and changes in the location of bond breaks. This possibility of characterizing the state of a specimen at various stages of a test may enable the measurement of bonding parameters with improved precision. Knowledge of the force-elongation curve parameters will also make possible the comparison of bonding parameters obtained from tests on samples of different densities.

Morphologies of the handsheets and constituent pulp fibers are being examined by scanning electron microscopy. Results of these investigations suggest that bonding in currency pulps may be due to the presence of a large fraction of fines which act as a "glue". These fines are not present in the wood pulps, and bonding between wood fibers depends on the ability of their surfaces to conform and establish intimate contacts at the junctions.

During the preparation process, pulp is subjected to mechanical action such as beating or refining. This treatment causes fibers to imbibe water and become more flexible, thereby facilitating interfiber conformation. However, the microstructure of the prepared pulp is influenced by the way in which water is bound to the fibers, and this varies with the kind of pulp material. This is being studied by measuring the proportions of bound and free water in different pulp samples.

The water imbibed by a pulp specimen is measured by solute exclusion. A dextran pulp specimen is added to a solution of dextran in water, and the excess water in the specimen dilutes the solution. The amount of the dilution is measured by polarimetry, and the imbibed water, or fiber saturation point, of the specimen is calculated. Part of the imbibed water is tightly bound to the cellulose and does not freeze at temperatures down to 223 K. This bound water fraction is measured by differential scanning calorimetry.

It is found that beating causes increasing amounts of water to be imbibed by both cotton and wood pulp fibers. However, beating causes an increasing fraction of the water imbibed to be

bound in cotton. This does not happen to as great an extent in wood pulp. It is believed that free water promotes flexibility and that bound water is attributed to breakdown of the crystalline structure. Thus, beating of wood pulp produces flexible conformable wood pulp fibers, but causes fibrillation and fines formation in cotton fibers.

Disorder in Drawn and Annealed Polyethylene

A. Peterlin, R. G. Snyder<sup>1</sup>, and J. R. Scherer<sup>1</sup>

In drawn high density polyethylene, the accordion type Raman scattering indicates the existence of extremely short chain stems. A possible interpretation is that they are not chain stems going through the whole crystal blocks from one fold surface to the next one, but straight chain stems between two gauche defects which interrupt the longitudinal accordion mode oscillation. If one may assume the existence of one such randomly located gauche defect per two chain stems in the crystal blocks of the drawn polyethylene, one can well represent the experimental data.

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

J. M. Cassel

Task Leader

The objective of this research is to contribute to dental health care through development of better performing materials and test methodology and standards appropriate thereto. Materials research and techniques are pursued with the goal of developing adhesive composite restorative materials of greater durability and wear resistance, and improved base metal alloy alternatives to the costly gold alloy prostheses. Knowledge of the structure and physical chemistry of biologically important calcium phosphates is used to develop improved preventive dental techniques. Improved test methodology is sought for characterization of the surfaces of surgical implant materials and for defining the interactions that occur thereon.

Dental research directions in support of the objective are established collaboratively with the American Dental Association, the National Institute of Dental Research, and the Department of Defense R&D command. Medical materials research is guided by close interaction with the Food and Drug Administration's Bureau of Medical Devices and the ASTM F-4 Committee (Medical and Surgical Materials and Devices).

Dental Composite, Resin, Sealant, and Cement Chemistry and Development

G. M. Brauer, J. M. Antonucci, J. W. Stansbury, R. E. Dehl, J. M. Cassel,  
R. L. Bowen<sup>1</sup>, H. Argentar<sup>1</sup>, D. W. Misra<sup>1</sup>, and T. Chen<sup>2</sup>

Current efforts are directed toward upgrading the quality of composite restorative materials with regard to color and storage stability, toxicity effects, adhesiveness, and durability. Structure-property relationships are developed and used as guides to the synthesis of new polymerization accelerators for dental resins. Laboratory synthesis and evaluation efforts have developed an amine accelerator with a reactivity that permits a threefold reduction in the concentration of accelerator required. The generic biocompatible nature of the amine, combined with the reduced concentration required, indicates that dimethylaminophenylacetic acid will prove a valuable dental resin component. Strong interest has been expressed by the dental manufacturers in a second amine developed to accelerate the curing of denture base materials without imparting any color. Efforts have continued to make a potentially very useful peroxide ascorbic acid copper initiator accelerator system more practicable. Invited papers covering initiator accelerator systems for acrylic resins and composites and new monomers for use in dentistry were presented at the Symposium on Biomedical and Dental Applications sponsored by the ACS in Houston.

The mechanism of reinforcement of dental composite restorative materials through silane inorganic fillers is being examined as a means of improving the durability of such materials when used in stress bearing applications. Bond formation between the silane coupling agent and the filler is monitored by infrared analysis and indicates that addition of selected amines to the carrier solvent improves the coupling effectiveness of the silane.

A major problem encountered in the investigation of the properties of dental composite restorative materials is the absence of quantitative analytical methods for determining chemical composition in the solid state. Infrared (IR) spectroscopy, which is widely used to analyze chemical composition, is useful for studying dental composites, but Fourier Transform capability is required because of light scattering and absorption by the glass filler. Measurements are currently being made with the new IR equipment of the Center for Materials Science. Recently we have performed some Raman spectroscopic analyses of dental composites and the various components of the composites, using the spectrometer in the Center. Preliminary results indicate that the Raman technique will circumvent many of the

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problems encountered with infrared analysis and will allow at least semiquantitative estimates to be made of chemical groups such as unreacted carbon/carbon double bonds in the polymerized composite matrix. Further work is in progress, as we use the Raman technique to analyze dental composite materials prepared by different experimental procedures. We are also investigating NMR as a means of studying the state of molecular motion in these presumably highly cross-linked resin systems. It is expected that the information thus obtained will be useful in evaluating the performance of dental materials.

At the request of the Council on Dental Materials, Instruments and Equipment of the American Dental Association, a status report for publication in the Association's Journal was prepared on the desirability of using radiopaque plastics in dentistry.

#### Development of Adhesive Bonding Technique

G. M. Brauer, R. L. Bowen<sup>1</sup>, J. M. Antonucci, D. W. Misra<sup>1</sup>,  
J. W. Stansbury, and J. M. Cassel

Strong mechanical bonding of acrylic resins to enamel surfaces can be obtained through acid etching of such surfaces, followed by resins or composite formulations capable of wetting and penetrating the newly created surfaces. Such treatment has not been applicable to surfaces of dentin and has not been entirely successful in the caries preventive application of pit and fissure sealants to the occlusal enamel surfaces of children's teeth.

One approach to adhesive bonding that is being pursued is the development of multi-functional molecules designed to interact with calcium on the tooth surface and with the in situ polymerizing dental resin. Using the diametral tensile strength of hydroxyapatite filled composites as a measure of the adhesiveness where the filler is coated with the coupling agent of interest, several surface active polymerization activators appear to offer promise.

One new direction taken recently has been the development of physiological buffer solutions capable of dissolving the smeared surface layers on cut dentin and of isotonic mordant solutions to improve bonding sites. Isotonic methacrylate monomer formulations containing adhesion promoting coupling agents have been developed that should not induce osmotic insult to odontoblasts and pulp tissues.

#### Wear Resistance and Mechanical Properties of Dental Materials

W. Wu, J. E. McKinney, J. M. Cassel, and E. Cobb<sup>2</sup>

In a study of the mechanisms governing both clinical and laboratory wear of dental restorative materials, a silver staining technique has been developed to examine structural changes in the damage zone immediately beneath the worn surface. Worn specimens are cross sectioned and examined by microscopy for quantification of the micro defects. Initially, clinically worn specimens are being provided through a guest worker from Georgetown University Dental School. The results to date suggest that greater efforts to introduce erosion effects into accelerated wear testing are required. Equipment to accomplish this has been designed and assembled.

With pin-on-disc wear instrumentation we have demonstrated that wear is very irregular, varying by a factor of two over different positions on the same specimen. The data support the use of durapatite, a form of sintered hydroxyapatite, as an appropriate substitute for human tooth enamel for in vitro measurements. However, microdefect analysis of in vivo and in vitro worn specimens brings into question the relevancy of in vitro data generated with enamel pins. The effect of loading on the accelerated wear results generated on dental composite specimens with hard (durapatite) and softer (steel) pins is under study. Initial transient wear regions indicate the presence of surface layers that inhibit wear of certain metals and alloys. These surface layers reform during periods of inactivity. Since this phenomenon may play a very important role in enhancing in vivo durability of amalgams and other dental alloys, efforts are in progress to determine surface compositions by means of Auger Electron Spectroscopy.

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## Auger Electron Spectroscopy (AES) Applied to Wear Analysis of Dental Alloys

J. E. McKinney, R. E. Dehl, and W. H. Grant

In vitro accelerated wear measurements on several dental alloys have been characterized by low initial wear rates followed by higher steady state rates of wear. We have attributed this behavior to the formation of a passive oxide surface layer, with higher wear resistance than the bulk material, that is reformed during periods of mechanical inactivity.

We have initiated examination of these surface layers by AES. Following a period to develop familiarity with the instrumentation (Surface Science Division, Center for Thermodynamics and Molecular Science) and confidence in the technique, measurements have been made on an amalgam, on three crown and bridge alloys, and on nickel as a standard. Preliminary measurements by argon ion sputtering of the surfaces to a depth of 10 nm has indicated distinct changes in composition as a function of depth into the surface layer. It is planned to generate AES depth profiles on a number of dental alloys with a goal of correlating surface layer analysis to the in vitro wear and finally to in vivo durability. Analysis of wearing surface layers may prove important for long term biocompatibility consideration including toxicity, chemical irritation, sensitization, and gingival inflammation from plaque.

### Porcelain Fused to Base Metal Alloys

J. A. Tesk, R. W. Hinman<sup>1</sup>, E. E. Parry<sup>1</sup>, and A. Holmes

This investigation is designed to develop knowledge of the physical, mechanical, and chemical properties of porcelain veneering alloys and their associated bonding porcelains relative to their use in cast crown and fixed partial dentures; to determine the effects of fabrication techniques on clinical serviceability of the restoration; to investigate factors affecting the bonding of porcelain to new dental alloys; and to determine potential methods for modification of fabrication techniques which may lead to improved clinical service. The chemical, physical, and mechanical properties of new, non-precious alloys are so different from those of the gold alloys that the application of the same fabrication techniques for porcelain bonding could be expected to be unsuccessful. This has proven to be the case, and not enough is yet known to render non-precious metal porcelain restorations as trouble free as gold porcelain restorations.

It is suspected that a major cause of porcelain metal failure resides in the residual stress which develops upon cooling of fired porcelain restorations. To address this problem, a multi-tiered approach has been taken: a) development of precise knowledge of the thermal expansion behavior and other mechanical and physical properties of porcelain and alloys after being subjected to dental laboratory firing conditions; b) the fabrication, according to dental laboratory fabrication procedures, of split ring composites of porcelain (opaque plus body) veneered to alloys and determination of the accompanying change in gap; c) the development of finite element model and elasticity analysis to examine the residual stress states and accompanying gap changes; and d) examination of porcelain and alloy for microstructural characteristics as well as examination of the microstructure of the porcelain alloy composite for stress induced (or other) flaws. Ultimately, the data developed in a) and b) will be used in the theoretical program in c) to determine the "macroscopic" residual stress states developed in the split ring. The analyses may further be developed with the knowledge developed in d), which may involve the superposition of microscopic stresses on the macroscopic stresses.

Results obtained thus far have shown that significant differences exist in expansion of porcelains which have received comparable levels of firing according to manufacturers' instructions. Differences exist between manufacturers' porcelains, and some develop significantly different expansions with repeated firing. Large differences in the amount of residual stress are fired into different porcelains, as indicated by the amount of stress relief which occurs.

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As compatibility depends not only on the stresses set up by differences in thermal contraction, but on geometrical shape and the thermal (or other) relief of stress, a split ring was conceived as presenting a reasonably close approximation to a clinical crown while providing a technique to assess the development of residual stress. Experimental and theoretical results of studies of gap and shape changes indicate that a previously derived mathematical expression is not sufficient to describe the complex interactions which exist and that discrepancies between theoretical and experimental results indicate stress relief at temperatures lower than  $T_g$ . These effects will be evaluated with refinements to finite element model and in view of the differences in crystallinity which have been shown to exist by Raman laser spectroscopic observations of the porcelains.

#### Dental Casting Alloys

J. A. Tesk, R. M. Waterstrat<sup>1</sup>, R. W. Hinman<sup>2</sup>, and E. E. Parry<sup>2</sup>

The commercial alloys now available for dental castings contain significant amounts of gold, silver, palladium, cobalt, nickel, and chromium. These metals formerly were abundantly available, but in recent years there have been sharp fluctuations in the price of these materials. It appears that the market for these metals will continue to be increasingly unstable, since there are no viable domestic sources of the ores, and the United States must import these metals from foreign countries which are susceptible to political or economic upheavals. The cost of these alloys is an important factor in dentistry; and in order to avoid future problems, it is prudent to plan some strategies to meet unexpected shortages or sharp increases in price. This can be accomplished by developing alternate alloys, and particularly those whose ores are available domestically. Titanium is an example of one such alternate. We have demonstrated that it is possible to produce precision dental castings based on titanium, but it is necessary to define the basic properties of these alloys before any laboratory castings can be produced for clinical use. During the past year, biocompatibility studies were completed on a titanium-13 percent copper alloy in cooperation with Dr. Frank Young at the Medical College of South Carolina. The results indicate that the alloy is very well tolerated in soft tissues. This is an important step toward eventual clinical trials in humans.

The ease with which a molten alloy fills the refractory mold cavity during the casting process is another problem that has been associated with the use of non-precious alloys. In an effort to ascertain the magnitude of this problem, an objective procedure for measuring the "castability" of dental alloys was developed as an early phase of this project and identified in a previous report. Early data resulting from this test method were plagued by unacceptably high variability. More recently, a modification of the pattern sprue has been tested, which results in much improved data. Using this procedural modification, extensive study has been undertaken to illustrate the differences in castability for various alloys when following the manufacturer's casting instructions. This work suggests that some non-precious alloys are relatively easy to manage in the laboratory. Early subjective clinical laboratory results appear to correlate quite well with measured values gathered in this project. The development of an objective technique to assess the correlation with margins on clinical crowns is desirable and will be pursued.

#### Dental Ceramics

C. P. Mabie<sup>1</sup>, D. L. Menis<sup>1</sup>, and R. L. Trout<sup>1</sup>

Work continues on the formulation of lower fusing dental porcelain frits prepared by the gel route. Frits have been made by the gel route which mature in a 12 minute air fire at 822 °C. These appear suitable for metal ceramic applications and have a thermal expansion greater than  $12 \times 10^{-6}/^{\circ}\text{C}$  between 23 and 400 °C. A high expansion rate is desirable to match those of some metals. The fusion or maturation temperature is 125 °C lower than the current lowest fusing commercial metal ceramic porcelain. Solubility of the low fusing porcelain is in the range of current commercial products. Deformation temperature under applied load is about 650 °C, the same as many other metal ceramic body porcelains.

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Other porcelain frits have been formulated which fuse at lower than 900 °C. Some of these have thermal expansions greater than  $14 \times 10^{-6}/^{\circ}\text{C}$  when measured between 23 and 400 °C. Solubilities tend to be high, but they are still within the commercial range. Many of these have very low deformation temperatures, i.e., the lowest temperature where stress between metal and ceramic may be relieved. Work continues on lowering the solubilities of these porcelains.

At least two dental companies have decided to experiment with gel route prepared frits. The gel route has potential for facilitating the introduction of nonradioactive phosphors to replace uranium in teeth.

### Irradiation Effects From Neutron Activated Dental Materials

J. A. Tesk

A potential source of radiation exposure which has not received direct attention involves secondary radiation from dental restorations activated by primary exposure to neutrons. This could present an additional hazard for the civilian and military personnel surviving exposure to a neutron bomb, for reactor operators and experimentalists suffering accidental exposure, for cancer patients receiving intense localized neutron radiation therapy, and others occupationally exposed to neutron radiation. Accordingly, calculations were made to estimate the additional dose of radiation ( $\beta + \gamma$ ) delivered to local oral tissues by neutron activated gold crowns. A primary 50 REM exposure was used as the baseline neutron exposure, as this clearly appears to be a complete survival dose for whole body exposure. For calculation purposes, a single gold crown of 2 grams was simulated by a disc 0.5 cm in radius and 0.14 cm thick located entirely on the buccal or lingual sides of a tooth to provide close approximation to soft tissue. We have concluded that secondary radiation doses from gold crowns activated by sublethal neutron fluences are comparable to the original dose from the neutrons. Results indicate that a 50 REM neutron dose would subsequently be accompanied by  $\sim 30$  REM. Higher primary neutron doses are followed by higher secondary doses (a high survival, whole body neutron dose of 200 REM is followed by  $\sim 120$  REM).

Dental or implant materials with major constituents behaving similarly to gold nuclei and irradiated by neutrons during cancer therapy will generate secondary doses comparable to the primary and must be duly considered. Long range effects of partial irradiation of an organ are not well known. For the levels presented, concern appears warranted for minimizing exposure. This research has been summarized in an article to be submitted to Medical Physics.

### Clinical and Laboratory Investigation of Dental Amalgams

N. W. Rupp<sup>1</sup>, G. C. Paffenbarger<sup>1</sup>, R. M. Waterstrat<sup>1</sup>, and R. Busby<sup>1</sup>

The reason for the progressive deterioration of amalgam restorations is a subject of intense interest although the theoretical understanding of this behavior is not well developed. Creep and corrosion are generally recognized as being important factors, but there is considerable controversy about the relative importance of these two factors, and it is possible that other significant factors have been overlooked.

Amalgam is a composite mixture of about six major constituents or "phases". The chemical and physical properties of such a mixture will depend on the properties of the individual phases, the percentage of each phase in the mixture, the size and shape of the crystals, and the properties of the interfaces between each phase. Thus, it is important to study the microstructures of each phase and to identify the tendencies for a chemical element to occur preferentially in certain regions of the microstructure. Elements such as tin, copper, manganese, and zinc are known to exhibit such behavior, and they produce important effects on the properties of the amalgam. These effects are being identified in a variety of experimental and commercial amalgams. An effort is then made to determine the relationships between the observed microstructure and the clinical behavior of the amalgams.

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<sup>1</sup>Research Associate, American Dental Association.



Currently, we are concentrating on the laboratory phase of the project. Dimensional changes are being observed for unrestricted specimens which have been stored in air at various temperatures for over three years. Seven pairs of alloys (zinc-containing paired with non-zinc-containing alloys of the same brand) have been under observation. All of the zinc-containing alloys made amalgams that continued to expand for the three years. The zinc-free amalgams all contracted. When one percent of powdered zinc was added to one of the non-zinc alloys, the change in dimension increased from  $-5 \mu\text{m}/\text{cm}$  for the non-zinc to  $+273 \mu\text{m}/\text{cm}$ . Thus, it would seem that zinc plays a role in the diffusion of mercury in hardened amalgam. This new knowledge of the role of zinc in the alloy may contribute to formula changes which could further improve the durability of amalgam restorations.

#### Dental Enamel Chemistry and Preventive Dental Treatments

W. E. Brown<sup>1</sup>, L. C. Chow<sup>1</sup>, M. Mathew<sup>1</sup>, G. L. Vogel<sup>1</sup>, M. Tung<sup>1</sup>,  
S. Takagi<sup>1</sup>, T. Gregory<sup>1</sup>, H. Heaton<sup>1</sup>, and P. Patel<sup>1</sup>

The objective of this project is to develop and apply fundamental information on the solubility and crystallographic structure of biologically important calcium-containing phosphate compounds to the development of improved dental caries preventive techniques. Important portions of this effort are concerned with 1) development of physicochemical models of the caries process to include insight into the mechanisms by which impurities and defects are incorporated into tooth enamel, and 2) application of solubility phase diagram analysis and kinetic data to the development of more effective enamel acid etch bonding treatments and improved topical fluoride procedures.

The structure of the following highly hydrated compounds has been determined:  $\text{MgNaPO}_4 \cdot 9\text{H}_2\text{O}$  and  $\text{Ca}_4\text{AlSi}(\text{SO}_4)\text{F}_{13} \cdot 12\text{H}_2\text{O}$ . These studies on some of the first known examples in which the phosphate ions are completely surrounded with water molecules provide a new structural basis for understanding chemical properties of the physiologically important phosphate ion in aqueous solutions.

For clinical application of fluoride in the past we have used a two-step process in which the tooth was first treated with  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ -forming solution, and then the  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  was converted to fluorapatite by a conventional fluoride solution. This procedure was shown to greatly increase the incorporation of permanently bound fluoride into enamel. We now have promising data for a new single step procedure which involves formation of  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  in the enamel. In vitro results showed that this procedure should be much more acceptable for clinical practice than a two-step procedure.

The use of relatively frequent mouth rinses with solutions containing low amounts of fluoride appears to be coming into favor over the use of infrequent treatments with concentrated solutions. We have made two in vitro studies in which a  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ -forming step is incorporated into the fluoride rinse procedure. The results from these studies showed that the permanent fluoride uptake by the enamel was significantly increased over a method currently used.

A new dental cement system comprising primarily calcium phosphate has been developed. At present, the cement has a compressive strength only about one-half that of ZnO cement and requires a setting time of about 15 minutes. Both the strength and setting time are expected to improve as the materials and procedures are modified. This cement has many potential applications in dentistry.

Progress in utilizing ultra-micro techniques to simulate and study the decay process has been made in several areas. This technique has produced, for the first time, information on calcium, phosphate, chloride concentration changes and the change in pH within enamel when the tooth specimen is undergoing a carious-like demineralization. This information provides important new insights into the mechanism of caries formation and has application to enamel remineralization processes as well.

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<sup>1</sup>Research Associate, American Dental Association.



R. E. Dehl and W. H. Grant

Two aspects of the adhesion of polymers to surfaces are of great importance in their many commercial applications as protective coatings, namely 1) the energy of adsorption of individual polymer molecules on the surface, which determines the adhesive strength of the film, and 2) the extent of surface coverage by the polymer, which determines the effectiveness of the adherent film in protecting the underlying substrate from chemical attack. We are presently investigating both aspects of this important problem by the use of radiolabelled polymers to study the adherence of the film and by Auger Electron Spectroscopy to study the uniformity of surface coverage by the polymer.

One measure of the energy of attachment or adhesive strength of polymers adsorbed on solid surfaces is the rate at which they become detached when the polymer-coated substrate is placed in contact with a suitable solvent. The desorption rate is affected both by the free energy of attachment of each segment of the polymer molecule with the surface and by the number of attached segments per molecule. The results of previous NBS studies, using radiolabelled polystyrene to detect the amount remaining on the surface, indicate that the rate of desorption decreases with increasing molecular weight of the polymer and with the amount of polymer initially adsorbed. Further experiments are in progress to quantitate these observations by systematically varying the amount of polymer initially adsorbed, followed by a careful study of the amount remaining after selected intervals of desorption. In this way, we expect to learn whether the polymer molecules which first arrive at the surface have a higher adsorption energy than the later arrivals, and whether such variables as the solvent used to deposit the film and the time spent in depositing a given amount of polymer on the surface significantly affect the adhesive strength of the film.

Auger Electron Spectroscopy (AES) is a technique for determining the elemental composition of the topmost 5-10 nm of a solid surface. The AES probe samples an area of about 20-80  $\mu\text{m}^2$  and can be used to determine variations in the surface chemical composition, given this lateral resolution. Preliminary AES experiments indicate that we can detect changes in the average thickness of a polymer film on a metal substrate as we scan across the sample. We expect to use the AES technique to study the uniformity of polymer film thickness as it is affected by the molecular weight of the polymer, the mass of polymer adsorbed per unit area, the time required to adsorb a given mass of polymer, and the molecular volume of the polymer molecules in solution prior to their adsorption. By studying the effect of each of these variables, we expect to gain insight into the optimum parameters for applying uniform polymer coatings to solid surfaces.

#### Characterization of Porosity of Porous Implant Materials

R. E. Dehl, W. H. Grant, A. Bur, and J. M. Cassel

The use of porous synthetic implant materials to serve as a scaffolding for the ingrowth of natural hard or soft tissue is a procedure utilized to stabilize selected medical implants. Characterization of the porosity of these materials is very important since the porosity governs their successful utilization. In cooperation with the Bureau of Medical Devices, Food and Drug Administration, a project has been initiated to survey published information and current commercial material specifications, perform void volume measurements on selected polymeric and composite materials by several alternative methods, and measure pore size distribution by optical intercept and mercury porosimeter techniques. In addition, the applicability of an experimental microparticle sieving technique, heretofore not applied to such systems, will be explored.

The accomplishments of this project's objectives will be of significance to the medical device industry, medical implant standards development, and ultimately, the users of porous implant materials.

## Dental and Medical Materials Standards

J. M. Cassel, G. M. Brauer, J. A. Tesk, N. W. Rupp<sup>1</sup>

Active participation, from Task Force level to the role of Subcommittee Chairman, occurs in development of dental standards through ANSI MD 156, Dental Materials, Instruments, and Equipment, and ISO TC 106, Dental Materials and Services. Development of medical implant standards is assisted by serving in roles of Polymeric Materials Chairman and Task Force leadership in the efforts of ASTM F-4, Medical and Surgical Materials and Devices, and as Chairman, USA TAG ISO TC 150, Surgical Implants.

### Investigation of Epitaxy Relationships Between $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ and Other Calcium Ortho-Phosphates

B. Dickens, L. W. Schroeder<sup>2</sup>

The purpose of this investigation was to examine possible epitaxies between  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$  (hydroxyapatite) and other calcium ortho-phosphates. These epitactical relationships are of interest for the following reasons: (i)  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$  may be considered as an idealization of the major inorganic phase in the human body, and its crystal chemistry obviously influences the properties of hard tissues, and (ii) epitactical relationships have been suggested to be important in explaining the apparent nonstoichiometry of  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$  and in the growth of biomineral in vivo.

Similarity in chemical content and periodicity of the chemical pattern between two planes in the component structures is an important requirement for epitaxy to occur under mildly forcing conditions. From the purely metric point of view, periodicity may be treated in terms of matching nets, one in each of the two components. In general, the metric fit of such nets will not be perfect, and the resultant misfit will be accommodated by lattice strain near the epitactical layer and/or by dislocations.

For the chemical aspects of epitaxy, structural features such as layers and corrugated sheets are prime candidates for the interfaces. Many structures contain layers in which the intra-layer bonds are strong and the interlayer bonds are weak. Especially in the case of inorganic salts, the atomic configurations in such layers will be relatively stable and, hence, can be expected to be found in more than one structure. The chemical pattern itself should not have a large motif, because this would have many structural details, and the probability of finding a similar motif in another compound would necessarily be low. From the above considerations, it follows that the most likely candidates for epitaxy-forming layers will be planes of low Miller indices of the form (100), (110), or (210), etc.

A filtering procedure for generating and quantitatively comparing possible cases of epitaxy and twinning in ionic compounds has been devised to provide quantitative criteria to evaluate the probability of epitaxy between compounds for which the crystal structures are known.

The two cornerstones of this procedure are:

- (i) Generate and examine in a systematic, quick manner all possible cases of epitaxy and twinning that may occur.
- (ii) Establish a relative probability of occurrence among the possible cases to delineate those requiring further study.

<sup>1</sup>Research Associate, American Dental Association.

<sup>2</sup>Guest worker, Food and Drug Administration.

Our approach is completely general in that it can be applied to any substance that forms a crystalline phase. Generation of possible cases of epitaxy or twinning which are specified in terms of contact planes requires only unit cell dimensions. Further evaluation of these cases in terms of atomic correspondences requires atomic positions. The procedure was used to evaluate the possibility of epitaxy between  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$  and other calcium orthophosphates. For any two given lattices, pairs of nets which match dimensionally within prescribed limits are found and sorted in order of increasing mismatch. The crystal structural parameters are used to generate and match atomic patterns corresponding to each pair of nets. Pattern matching is done by comparing magnitudes of vectors describing the immediate environment of representative atoms in the two patterns. Atomic charges related by each vector are also considered. Use of the vector sets introduces the limitation that twinning involving reorientation in a contact plane cannot be distinguished from no reorientation. The procedure is general in nature and has been applied to the study of possible epitaxies between  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$  and  $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ ,  $\text{Ca}_4\text{O}(\text{PO}_4)_2$ ,  $\text{CaHPO}_4$ ,  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ ,  $\beta\text{-Ca}_3(\text{PO}_4)_2$ , and  $\text{Ca}_5(\text{PO}_4)_2\text{SiO}_4$ .

The highest probabilities for epitaxy are between  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$  and  $\text{Ca}_8(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ ,  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$  and  $\text{Ca}_4\text{O}(\text{PO}_4)_2$ , and  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$  and  $\text{Ca}_5(\text{PO}_4)_2\text{SiO}_4$ . Of these, the first is the most likely and is probably unavoidable under conditions where  $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$  is stable, and the last is the least likely. Possible epitaxies between  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$  and  $\text{CaHPO}_4$  or  $\beta\text{-Ca}_3(\text{PO}_4)_2$  are less likely than epitaxy between  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$  and  $\text{Ca}_4\text{O}(\text{PO}_4)_2$ .

Although  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  had been suggested to be important in tooth mineralization, evaluation of the probability of epitaxy in these cases suggests that any deposition of these phases on one another forms incoherent films which then mechanically block access of the surrounding solution to the interior and that epitaxial growth is not important. Therefore, among those cases considered, only the epitaxies  $\text{Ca}_5(\text{PO}_4)_3\text{OH}/\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$  and  $\text{Ca}_5(\text{PO}_4)_3\text{OH}/\text{Ca}_4\text{O}(\text{PO}_4)_2$  appear likely to occur in practice.

#### Development of Improved Field Dental Composite Restorative Materials for Military Dentistry

G. M. Brauer, N. Rupp<sup>1</sup>, K. Dermann<sup>2</sup>, J. Stansbury, J. Cassel

Current thrust of this continuing project is to provide guidelines to the Army regarding materials and techniques for addressing the problem of poor marginal adaptation that frequently occurs with composite restorative materials. Resultant marginal staining and leakage compromises the aesthetic advantages of these restorations and can reduce their service life.

The role of polymerization shrinkage, coefficient of thermal expansion, nature of filler, and properties of diluent monomers are being investigated. Efforts are being made to establish optimum minimum levels of viscosity-modifying diluent monomers that will produce adequate working characteristics and physical properties, while at the same time reducing the polymerization shrinkage that occurs on hardening. Radiotracer techniques are employed to ascertain leakage around class V restorations placed in extracted caries-free teeth.

<sup>1</sup>Research Associate, American Dental Association.

<sup>2</sup>Guest worker, Free University of Berlin.



## Other Division Activities

### Invited Talks

The Accelerative and Adhesive Bonding Capabilities of Surface Active Accelerators  
International Association for Dental Research, Osaka, Japan

J. M. Antonucci

June 6, 1980

Ferroelectric Polarization in Polymers

International Symposium on the Statistical Mechanics of Phase Transitions in  
Polymers, Case Western Reserve University, Cleveland, Ohio

M. G. Broadhurst

June 13, 1980

Piezoelectric and Pyroelectric Applications of Plastics

American Chemical Society, Houston, Texas

M. G. Broadhurst

March 24, 1980

Piezoelectric and Pyroelectric Properties of Polymers With Applications

International Business Machines, Binghamton, New York

M. G. Broadhurst

January 28, 1980

Piezoelectric Polymers

Office of Naval Research Meeting on Electroactive Polymers, Washington, D.C.

M. G. Broadhurst

September 29, 1980

Polarization and Molecular Hysteresis in Polyvinylidene Fluoride

Gordon Conference on Dielectric Phenomena, New London, New Hampshire

M. G. Broadhurst

July 19, 1980

Polymers as Piezoelectric Elements

Plastics Institute of America, Hoboken, New Jersey

M. G. Broadhurst

November 1, 1979

Recent Developments With Piezoelectric Polymers

Polymer Chapter of the 3M Company Technical Forum, St. Paul, Minnesota

M. G. Broadhurst

June 16, 1980

Ferroelectric Polarization in Polymers

Conference on Electrical Insulation and Dielectric Phenomena, White Haven,  
Pennsylvania

M. G. Broadhurst and G. T. Davis

October 24, 1979

Ferroelectric Polarization in Polymers

American Physical Society, New York, New York

M. G. Broadhurst and G. T. Davis

March 27, 1980

Poling Behavior of PVDF

American Physical Society, New York, New York

M. G. Broadhurst and G. T. Davis

March 24, 1980

Derivatives of p-N,N-Dialkylaminophenylalkanoic Acid: New Accelerators for Dental Composites

International Association for Dental Research, Osaka, Japan

G. M. Brauer

June 6, 1980

Enhancing Fluoride Incorporation into Enamel

School of Dentistry, National Taiwan University, Taipei, Taiwan

W. E. Brown

June 16, 1980

Impregnation and Void Filling of Porous Polymer Tape With Dielectric Oil  
Conference on Electrical Insulation and Dielectric Phenomena, White Haven,  
Pennsylvania

A. J. Bur

October 23, 1979

The Development of Test Methods for the Environmental Stress-Crack  
Resistance of Ethylene Plastics

ASTM Subcommittee D-20.10.14, San Diego, California

J. M. Crissman

February 19, 1980

Piezoelectric and Pyroelectric Polymers: Mechanisms and Applications  
University of Virginia, Charlottesville, Virginia

G. T. Davis

January 28, 1980

Piezoelectric and Pyroelectric Polymers: Mechanisms and Applications

Mechanics and Materials Colloquia, Rutgers University, New Brunswick, New Jersey

G. T. Davis

April 24, 1980

Piezoelectric Polymer Research at NBS

Piezoelectric Polymer Workshop, Naval Research Laboratory, Orlando, Florida

G. T. Davis

June 13, 1980

Piezo- and Pyroelectric Response From PVDF in Form III ( $\gamma$ )

American Physical Society, New York, New York

G. T. Davis and M. G. Broadhurst

March 24, 1980

Non-Uniform Polarization and Space Charge in Ferroelectric Polymers

American Physical Society, New York, New York

A. S. DeReggi and M. G. Broadhurst

March 24, 1980

Temperature Dependence of the Pyroelectric Response and Thermal Depoling  
of Vinylidene Fluoride Polymer

American Physical Society, New York, New York

A. S. DeReggi, G. T. Davis, and M. G. Broadhurst

March 24, 1980

Crystal Disorders in Copolymers of Tetrafluoroethylene and Hexafluoropropylene  
Institute of Polymer Chemistry, Zabrze, Poland

R. K. Eby

October 26, 1979

Order-Disorder Transitions in Polytetrafluoroethylene: Experiment and Theory  
Institute of Basic Technical Problems, Warsaw, Poland

R. K. Eby

October 22, 1979

Overview of NBS and the Polymers Division  
E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware  
R. K. Eby  
April 2, 1980

Polymers in the Future  
American Society for Mechanical Engineers Emerging Technology Conference,  
San Francisco, California  
R. K. Eby  
August 15, 1980

The Structure and Transitions in Copolymers of Tetrafluoroethylene  
and Hexafluoropropylene  
Polish Academy of Sciences, Lodz, Poland  
R. K. Eby  
October 24, 1979

Crystal Disorders in Copolymers of Tetrafluoroethylene and Hexafluoropropylene  
American Chemical Society, Washington, D.C.  
R. K. Eby, E. S. Clark, and J. J. Weeks  
September 12, 1979

Measurement of Dynamic Elastic Moduli  
99th Acoustical Society, Atlanta, Georgia  
S. Edelman  
April 22, 1980

Raman Frequencies and Intensities of Longitudinal Acoustic Modes of Polymers  
University of Massachusetts, Amherst, Massachusetts  
B. M. Fanconi  
September 21, 1979

Application of Varied Heating Rate Methods to Polymer Degradation Reactions  
Ninth North American Thermal Analysis Society Conference, Chicago, Illinois  
J. H. Flynn  
September 25, 1979

Lifetime Prediction of Polymer Stabilization  
Institute of Polymer Science and Technology, University of New York,  
New Paltz, New York  
J. H. Flynn  
June 27, 1980

Methods for Testing the Validity of Kinetic Models Using Data From Varied  
Heating Rate and Jump Techniques  
American Chemical Society, Seton Hall Univ., South Orange, New Jersey  
J. H. Flynn  
February 25, 1980

Methods for Testing the Validity of Kinetic Models Using Data From Varied  
Heating Rate and Jump Techniques  
Sixth International Conference on Thermal Analysis, Bayreuth, West Germany  
J. H. Flynn  
July 8, 1980

Concentration Effect on Polymer Chain Dimensions  
Joint U.S.-France Conference on Small Angle Scattering, Strasbourg, France  
C. C. Han  
September 17, 1980



Dynamic Scattering From Polymer Solutions  
University of Michigan, Ann Arbor, Michigan  
C. C. Han  
October 5, 1979

Molecular Weight and Temperature Dependence of Polymer Dimensions and Intrinsic Viscosity  
University of Massachusetts, Amherst, Massachusetts  
C. C. Han  
February 15, 1980

Experiments on Non-Linear Elasticity  
Short Course on Continuum Mechanics, NBS, Gaithersburg, Maryland  
E. A. Kearsley  
July, 1979

Non-Equilibrium Thermodynamics of Perfect Elastic Fluids  
Seminar on Thermodynamic Inequalities, NBS, Gaithersburg, Maryland  
E. A. Kearsley  
July 17, 1980

The Diversity in the Habits Exhibited by Polymer Crystals Grown From Solution  
Leeds University, Leeds, England  
F. A. Khoury  
October 2, 1979

Diversity in the Lateral Growth Habits and Non-Planar Character of Polyethylene Crystals  
Bell Telephone Laboratories, Murray Hill, New Jersey  
F. A. Khoury  
February 21, 1980

Overview of Investigations in the Polymers Division on "The Structure and Dielectric Properties of Polymer Tape Insulation for High Power Transmission Cables"  
Battelle Laboratories, Columbus, Ohio  
F. A. Khoury  
December 6, 1979

Scanning Transmission Electron Microscopy of Polyethylene Crystals  
Electron Microscopy Society of America, Reno, Nevada  
F. A. Khoury  
August 4, 1980

A Mean Field Theory of Polymer Solutions  
Polytechnic Institute of New York, Brooklyn, New York  
D. J. Lohse  
April 15, 1980

Concentration Dependence of Polymer Chain Dimensions  
Johns Hopkins University, Baltimore, Maryland  
D. J. Lohse  
January 30, 1980

Dependence of Polymer Chain Dimensions on Concentration  
E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware  
D. J. Lohse  
February 18, 1980

Dependence of Polymer Chain Dimensions on Concentration  
Hercules Corporation, Wilmington, Delaware  
D. J. Lohse  
February 21, 1980

Dependence of Polymer Chain Dimensions on Concentration  
Kansas State University, Manhattan, Kansas  
D. J. Lohse  
April 4, 1980

Statistical Mechanics of Polymer Solutions  
Exxon Chemical Co., Linden, New Jersey  
D. J. Lohse  
April 8, 1980

A History of the Society of Rheology  
Fiftieth Anniversary Meeting of the Society of Rheology, Boston, Massachusetts  
R. S. Marvin  
October 29, 1979

Cyclic Creep and Failure of Carbon Black Filled Rubber  
IBM Research Laboratories, San Jose, California  
G. B. McKenna  
May 9, 1980

Mechanical Durability and Failure of Polymeric Materials  
Free University, Amsterdam, Netherlands  
G. B. McKenna  
April 14, 1980

Non-Linear Viscoelastic Behavior of PMMA in Torsion  
Bell Telephone Laboratories, Murray Hill, New Jersey  
G. B. McKenna  
October 26, 1979

Response of Carbon Black Filled Rubber to Cyclic Loading  
Malaysian Rubber Products Research Association, Brickendonberry, England  
G. B. McKenna  
April 18, 1980

Time Dependent Deformation and Failure Behavior of Poly(Methyl Methacrylate) and Polyethylene  
University of Leeds, Leeds, England  
G. B. McKenna  
April 17, 1980

Time Dependent Failure in PMMA and Polyethylene  
University of Manchester Institute of Science and Technology, Manchester, England  
G. B. McKenna  
April 16, 1980

Research and the Saving of Teeth  
Tokyo Medical and Dental University, Tokyo, Japan  
G. C. Paffenbarger  
May 30, 1980

Research and the Saving of Teeth  
Taiwan University of Dentistry, Taipei, Taiwan  
G. C. Paffenbarger  
June 13, 1980

Acoustic Emission of Polymers During Crazeing  
American Physical Society, New York, New York  
A. Peterlin  
March 27, 1980

Elastic Modulus and Strength of Highly Drawn Polymers  
Dutch Staatsmijnen, Geelen, Holland  
A. Peterlin  
October 26, 1979

Molecular Interpretation of the Load-Elongation Curve of Crystalline Polymers  
ACS Symposium on Stress-Cracking of Plastics, Washington, D.C.  
A. Peterlin  
September 14, 1979

Polymer Coil Instability in Laminar Flow  
American Chemical Society, Carnegie-Mellon University, Pittsburgh, Pennsylvania  
A. Peterlin  
February 28, 1980

Tensile Failure of Semicrystalline Polymers  
U.S.-Japan Meeting on Crazing, Flow, and Forming of Polymers, Rutgers University,  
New Brunswick, New Jersey  
A. Peterlin  
May 21, 1980

Transport Phenomena and Polymer Morphology  
IUPAC Symposium on Polymers, Mainz, West Germany  
A. Peterlin  
September 18, 1979

Transport Phenomena and Polymer Morphology  
Laboratory Technology of Polymers and Rheology, Naples, Italy  
A. Peterlin  
October 23, 1979

Transport Phenomena in Drawn Semicrystalline Polymers I  
Laboratory Technology of Polymers and Rheology, Naples, Italy  
A. Peterlin  
May 7, 1980

Transport Phenomena in Drawn Semicrystalline Polymers II  
Laboratory Technology of Polymers and Rheology, Naples, Italy  
A. Peterlin  
May 12, 1980

Type II Diffusion in Glassy Polymers  
Laboratory Technology of Polymers and Rheology, Naples, Italy  
A. Peterlin  
October 19, 1979

Polymer Morphology and Chain Transport Mechanisms  
Boris Kidric Institute of Nuclear Sciences VINCA, Beograd, Yugoslavia  
D. H. Reneker  
September 25, 1979

Properties of Polymers Including Chain Transport and Piezoelectric Effects  
Josef Stefan Institute, Ljubljana, Yugoslavia  
D. H. Reneker  
September 28, 1979

Dental Materials--Their Selection and Handling Techniques in 1979-80  
Travis Air Force Base, Solano, California  
N. W. Rupp  
September 5, 1979



Dental Materials--Their Selection and Handling Techniques in 1979-80  
Scott Air Force Base, Saint Clair, Illinois  
N. W. Rupp  
September 12, 1979

Operating Techniques With Recently Introduced Dental Materials  
University of West Virginia, Morgantown, West Virginia  
N. W. Rupp  
September 21, 1979

Recent Developments in Dental Materials and Their Handling Techniques  
Lackland Air Force Base, San Antonio, Texas  
N. W. Rupp  
September 27, 1979

Seminar on Clinical Research  
University of Minnesota, Minneapolis, Minnesota  
N. W. Rupp  
September 18, 1979

Equation of State Theories of Polymer Blends  
International Symposium on Polymer Compatibility and Incompatibility, Michigan  
Molecular Institute, Midland, Michigan  
I. C. Sanchez  
August 18, 1980

Interfacial Tension Theory of Polymer Solutions  
University of Washington, Seattle, Washington  
I. C. Sanchez  
March 18, 1980

Phase Diagrams of Polymer Alloys  
Washington State University, Pullman, Washington  
I. C. Sanchez  
March 19, 1980

Phase Diagrams of Polymer Blends  
Great Lakes Polymer Conference, Wayne State University, Detroit, Michigan  
I. C. Sanchez  
February 14, 1980

Phase Equilibrium Behavior of Polymer Blends  
University of Akron, Akron, Ohio  
I. C. Sanchez  
December 6, 1979

Statistical Mechanical Models of Interacting Polymer Chains  
NBS Colloquium on Mathematical Modeling in Science and Engineering, Gaithersburg,  
Maryland  
I. C. Sanchez  
February 20, 1980

Statistical Mechanical Models of Polymers and Their Solutions  
Massachusetts Institute of Technology, Cambridge, Massachusetts  
I. C. Sanchez  
November 7, 1979

Statistical Mechanical Models of Polymers and Their Solutions  
Michigan Molecular Institute, Midland, Michigan  
I. C. Sanchez  
February 15, 1980

Statistical Mechanics of Dilute and Semi-Dilute Polymer Solutions  
Carnegie-Mellon University, Pittsburgh, Pennsylvania  
I. C. Sanchez  
May 2, 1980

Statistical Thermodynamics of Polymer Solutions  
Johns Hopkins University, Baltimore, Maryland  
I. C. Sanchez  
March 5, 1980

Theory of Polymer Interfacial Tension  
E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware  
I. C. Sanchez  
February 14, 1980

Diffusion and Determination of Chain Structure in Polymers  
Georgetown University, Washington, D.C.  
L. E. Smith  
November 7, 1979

Re-Evaluation of the Safety of Plastics  
North Carolina State University, Raleigh, North Carolina  
L. E. Smith  
April 9, 1980

Dental Alloy and Ceramic Compatibility  
International Precious Metals Institute, Toronto, Canada  
J. A. Tesk  
June 2, 1980

Application of Solid State  $^{13}\text{C}$  NMR in Semicrystalline Polymers  
Firestone Tire & Rubber Co., Akron, Ohio  
D. L. VanderHart  
December 20, 1979

$^{13}\text{C}$  Linewidths in Solid Polymers Using High-Power Proton Decoupling and  
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Field H. Winslow  
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B. B. Djordjevic  
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Carolyn K. Purvis  
NASA-Lewis Research Center, Cleveland, Ohio  
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Bruce Banks  
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Paul Mentag  
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July 22, 1980

Studies of Polymer Conformations in Solid Polymers by Small and Wide Angle Neutron Scattering  
Jakob Schelten  
Institut für Festkörperforschung, Jülich, West Germany  
August 13, 1980



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<b>4. TITLE AND SUBTITLE</b> Polymer Science & Standards Division Annual Report 1980			
<b>5. AUTHOR(S)</b> R. K. Eby, M. G. Broadhurst, J. M. Cassel, B. M. Fanconi, I. C. Sanchez, L. E. Smith			
<b>6. PERFORMING ORGANIZATION</b> <i>(If joint or other than NBS, see instructions)</i>  <b>NATIONAL BUREAU OF STANDARDS</b> <b>DEPARTMENT OF COMMERCE</b> <b>WASHINGTON, D.C. 20234</b>		<b>7. Contract/Grant No.</b>	<b>8. Type of Report &amp; Period Covered</b>
<b>9. SPONSORING ORGANIZATION NAME AND COMPLETE ADDRESS</b> <i>(Street, City, State, ZIP)</i>			
<b>10. SUPPLEMENTARY NOTES</b>  <input type="checkbox"/> Document describes a computer program; SF-185, FIPS Software Summary, is attached.			
<b>11. ABSTRACT</b> <i>(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)</i>  This publication outlines the organization and programs of the Polymer Science and Standards Division of the National Bureau of Standards. It contains summaries of all technical projects in the Division for the 1980 fiscal year.			
<b>12. KEY WORDS</b> <i>(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)</i> polymers, plastics, macromolecules, standards			
<b>13. AVAILABILITY</b> <input checked="" type="checkbox"/> Unlimited <input type="checkbox"/> For Official Distribution. Do Not Release to NTIS <input type="checkbox"/> Order From Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.  <input checked="" type="checkbox"/> Order From National Technical Information Service (NTIS), Springfield, VA. 22161		<b>14. NO. OF PRINTED PAGES</b>  81  <b>15. Price</b>	







