Meetings

Deformation and Fracture of High Polymers

The 1972 Battelle Colloquium on Deformation and Fracture of High Polymers was held in Kronberg, Germany, at a resort in the Taunus mountain range near Frankfurt, from 11 to 16 September 1972 (*1*). The proceedings of the meeting (*2*) will be dedicated to Herman F. Mark of Brooklyn Polytechnic Institute, who has been active in polymer science practically from its beginning and has contributed to nearly all of its fields, from reaction kinetics to x-ray diffraction, and from the study of phase transitions to graft-copolymerization and biomedical application of new polymeric materials.

In the early years of polymer science the development of new polymeric materials dominated the scene. In recent years new polymerization techniques, new classes of monomers, and new structural concepts enhanced the variety and versatility of polymer products, and especially improved the properties of polymers for engineering use. With the help of strong, stiff reinforcing fibers, polymeric materials now perform well beyond the old limits of performance. What are these limits and what are their causes? In connection with this problem, questions such as the following arise:

- What are the relations between the structure and mechanical properties of high polymers in the crystalline, rubbery, and glassy states?
- How does the molecular structure of a polymer influence its rheological behavior?
- What are the effects on mechanical behavior of introducing coherent (compatible) and incoherent (incompatible) phases?
- What are the proper phenomenological approaches to constructing constitutive relations?
- Can these phenomenological methods provide a basis for developing viable theories of deformation and fracture?
- How can multiaxial stresses, particularly those at the tip of a crack, be taken into account in these descriptions?

Problems of such complexity are best considered by an interdisciplinary forum, such as the Battelle Colloquium. The topic was considered from three disciplinary viewpoints: the macroscopic viewpoint of continuum mechanics, the microscopic viewpoint of solid-state physics and metallurgy, and the molecular viewpoint of polymer science.

Six introductory lectures provided historical background on the subject. These covered the synthesis and application of polymers (Mark), deformations and molecular motions above the glass transition temperature (Ferry), the interconversion of linear viscoelastic functions applied to shear behavior in the glass-rubber transition region (Schwarzl), materials with memory (Rivlin), and mechanical behavior of high polymers (Alfrey). The introductory paper of Barenblatt on methods of combustion theory in the mechanics of deformation, flow, and fracture of polymers was read by Kanninen.

The following 4 days were devoted to sessions on subfields of the main theme. The session on phenomenology was chaired by Tschoegl. Rubberlike behavior (Becker), plastic deformation of polymers (Landel), and flow under high pressure (Radcliffe) were reported. The stress-strain curves as a function of strain rate, temperature, and pressure (the variables in the equation of state) were discussed with the objective of finding generalized descriptions and separating the apparently complex stress-strain behavior into simpler competing processes.

Particular attention was directed to the process of craze formation. A new technique of transmission electron microscopy that has permitted the observation of substrate-free polymer crystals was described (Gleiter). Polyethylene crystals subjected to stress normal to the axis of the chain fail in a brittle manner even if the experiment is carried out at a temperature close to the melting point. As a result of crystal cracking, fibers are drawn out across the crack in a two-step process: in the first step, single blocks of folded chains are broken off the crystallite, and in the second step a thermally activated rearrangement of the molecules occurs. Hull discussed the microstructure and the stress-strain response of crazes formed in bulk polystyrene. He viewed crazing in the context of crack formation and the state of stress ("normal" and "shear"). In polystyrene failure is preceded by crazing: nucleation and propagation of a crack can be interpreted in terms of the deformation and failure of fibrils. The latter statements were supported by Menges, who proposed that crazes are initiated through adhesive failure at intergranular boundaries within the sample, rather than failure along slip planes or domain boundaries.

The third session, chaired by Müller, was devoted to molecular descriptions of deformation. Molecular processes in deforming polymers were compared with those in crystalline solids, where deformation is controlled by the motion of dislocations (Li, Shen, Pechhold). The results of electron spin resonance (ESR) investigations of the stress-induced chain scission process and the role of intermolecular cohesion in chain scission were discussed (Andrews, Kausch). The influence of chain scission and of the free radicals thus formed on fracture initiation is still disputed. Two theories have been advanced: in one free radicals trigger the formation of microcracks and macroscopic deformation, and in the other free radicals are simply a by-product of local deformation within a sample. Electron spin resonance investigations are of importance in evaluating the validity of these theories. The stress transmission lengths (20 to 50 Å in crystallites and more than 300 Å in amorphous regions) have a strong bearing on when and where to apply continuum treatment of crack growth. Vincent described other structural changes at the tip of a crack and related them to the distribution of stress and strain in that area, the shape of

load extension curves, and fracture toughness.

The description of deformation of an ensemble of statistically interacting particles which appears to be smooth in time and space was the topic of the session on continuum descriptions of deformation, chaired by Lee. The behavior of viscoelastic solids and solutions in extrusion, compression, and tension was discussed (Takayanagi, Zapas, Brinson, Rybicki). Anthony developed the concept of disclinations, a geometrical tool to describe certain polymer defects (for example, twist and wedge disclinations), by using the methods of continuum theory. From such continuum treatments, a relation between microstructure and the elastic and plastic behavior of polymers may be expected.

The session on fracture was chaired by M. L. Williams. Fracture propagation (Kanninen, Kobayashi) and conditions of crack stability and the relation between viscoelastic functions and crack extension parameters (Thomas, Knauss) were discussed. Knappe treated the role of fracture criteria in the fracture analysis of fiber-matrix composites. J. G. Williams took up the previously discussed problem of craze formation, subjecting it to fracture mechanical analysis. He also studied the effect of temperature and environment.

After each paper, time for direct questions was allowed. A 3-hour agenda discussion of the topic of the morning session concluded every day.

Some of the accomplishments of the colloquium have been indicated in the brief comments on the individual sessions. The presentation of the closely related papers provided a high information density, and all conceivable arguments from the three disciplinary viewpoints were advanced and discussed. In illustration, we may mention crazing. Environmental effects on craze initiation are undisputed. But what is their nature? The solubility parameter seems to be an insufficient criterion. Hydrogen bonding, sample orientation, swelling, wetting, presence of minute impurities, and diffusion all have to be considered. Gases can adsorb on carbon-carbon bonds and reduce the bond energy, and facilitate chain scission, the opening of voids, and crack initiation. The exposition and interaction of these interdisciplinary viewpoints is a major accomplishment of the colloquium; subsequent evaluation by participants (and readers) will be an even greater one.

Another illustration is the problem of crack branching and its relation to dynamic toughness. Is the energy or the shape of the stress field at the crack tip important? Is it the decoupling of stress field and crack propagation or the statistical chance that off-axis flaws will grow to sufficient size that determines deviations of crack propagation from one plane and crack branching? The arguments were presented in an elegant fashion. They are well founded, and they will be taken up again. These few examples show the breadth of the discussion, which extended from the mathematical foundations of viscoelasticity to the thermodynamic formulation of fracture and design criteria.

A summarizing discussion on critical issues that remain to be resolved, chaired by Halpin, concluded the 7-day meeting in the pleasant setting of the Schlosshotel Kronberg.

H. H. KAUSCH
Battelle-Institut, e.V.,
Frankfurt/Main, Germany
J. A. HASSELL
R. I. JAFFEE
Battelle Columbus Laboratories,
505 King Avenue,
Columbus, Ohio 43201

References and Notes

1. Participants at the colloquium cited in this report are H. F. Mark (Brooklyn Polytechnic Institute, Brooklyn, New York); J. D. Ferry (University of Wisconsin, Madison); F. R. Schwarzl (TNO, Delft, Holland); R. S. Rivlin (Lehigh University, Bethlehem, Pennsylvania); T. Alfrey (Dow Chemical Company, Midland, England); G. I. Barenblatt (Moscow University, Moscow, U.S.S.R.); M. F. Kanninen (Battelle Columbus Laboratories, Columbus, Ohio); N. W. Tschoegl (California Institute of Technology, Pasadena); G. W. Becker (Bundesanstalt für Materialprüfung, Berlin, Germany); R. F. Landel (California Institute of Technology); S. V. Radcliffe (Case Western Reserve University, Cleveland, Ohio); H. Geiter (Ruhr Universität, Bochum, Germany); D. Hull (University of Liverpool, Liverpool, England); G. Menges (Institut für Kunstoffverarbeitung, Aachen, Germany); F. H. Müller (Institut für Polymere der Universität Marburg, Marburg, Germany); J. C. M. Li (University of Rochester, Rochester, New York); M. C. Shen (University of California, Berkeley); W. Pechhold (Universität Ulm, Stuttgart, Germany); E. H. Andrews (Queen Mary College, London, England); H. H. Kausch (Battelle-Institut, e.V., Frankfurt/Main, Germany); P. C. Vincent (Imperial Chemical Industries, Ltd., Hertfordshire, England); E. H. Lee (Stanford University, Stanford, California); M. Takayanagi (Kyushu University, Kyushu, Japan); L. Zapas (National Bureau of Standards, Gaithersburg, Maryland); H. F. Brinson (Virginia Polytechnic Institute, Blacksburg); E. F. Rybicki (Battelle Columbus Laboratories); K. H. Anthony (Universität Stuttgart, Stuttgart, Germany); M. L. Williams (University of Utah, Salt Lake City); A. S. Kobayashi (University of Washington, Seattle); A. G. Thomas (Natural Rubber Producer's Research Association, Welwyn Garden City, Hertfordshire, England); W. G. Knauss (California Institute of Technology); W. Knappe (Deutsches Kunststoff-Institut, Darmstadt, Germany); J. G. Williams (Imperial College, London, England); J. C. Halpin (Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio).
2. H. H. Kausch, J. A. Hassell, R. I. Jaffee, *Deformation and Fracture of High Polymers* (Plenum, New York, in press).