

Preface

Polymer science and engineering as a discipline is some fifty years old. This brief lifetime has seen the development of synthetic elastomers that equal or exceed nature's product, Hevea rubber, in abrasion resistance, tensile strength, high temperature performance, and degradation resistance; the development of a molecular theory of rubber elasticity, truly a triumph of statistical mechanics; the development of synthetic fibers that now clothe a significant fraction of the world's population; the emergence of plastics as structural or protective elements for the sheltering of man; the use of polymeric films and materials for artificial hearts, kidneys and blood dialysis; the synthesis of stereospecific polymers which come close to the duplication of nature in chemical modeling; and countless other areas where low density, optical clarity, dielectric activity (or the lack of it), corrosion resistance, biological inertness, ease of fabrication, or other specific properties dictate the use of high polymers.

Whereas polymer organic chemistry represented the major academic endeavor during the early years of macromolecular science, the last twenty years have indicated a trend toward the emphasis of polymer physics and physical chemistry. The last several years give clear indication that a major re-emphasis is about to occur once again in that the field of polymer engineering is beginning to emerge. Industry has a clear need for engineers and scientists versed in the engineering sciences but with expanded knowledge of the properties and processing of polymers. In particular, problems associated with the failure of polymers, such as the engineering properties of fracture, creep resistance, impact strength, fatigue and solvent stress cracking and crazing are numerous and difficult.

The statistical structure of polymeric glasses and the broad spectrum of order-disorder and morphology in "crystalline" polymers have yet to be quantified to the degree to which defects such as vacancies and dislocations have been quantified for metals. This, together with the strong dependence of polymer solid properties on the melt rheology and history, as compared to the weak dependence of metal properties on melt history, makes the relationships between failure properties and "structure" of polymeric solids difficult and often elusive. As is well known, small but significant changes in orientation of the solid resulting from changes in melt flow field (e.g. by changes in die design) can lead to greatly improved or reduced tensile strength or impact strength.

What is clear is that specification of the structure is far more complex than a delineation of chemical composition, tacticity, molecular weight and so forth. Recent studies on glassy polymers have shown that thermal history is a primary variable for these non-equilibrium materials. However, the extent to which gross or subtle changes in morphology as induced by the stress, strain, temperature and flow histories of the solid and melt precursor affect the ultimate properties of the solid remains to be delineated. As polymers are used with increasing regularity in structural engineering components, it will become of major importance both to control their properties through a more thorough understanding of the relevant structural parameters of the final solid object and to design (in the engineering context) with meaningful me-

chanical properties data which reflect the strongly time, temperature and stress state and level dependent properties which polymers exhibit.

The three articles which appear in this volume represent distinct, but complementary aspects of the general theme of failure in polymers. Professor Andrews has summarized research on the molecular failure mechanism itself as reflected in radical formation which occurs during chain scission. As he points out there is considerable difficulty in correlating directly the rate of radical formation with the applied stress or strain levels and time histories. In part this is due to experimental difficulties associated with performing stress-strain experiments in the spectrometer cavity. A number of the studies reported were, unfortunately, not very specific as to the sample stress or strain and loading history. Furthermore, catastrophic failure as embodied in the fast propagation of a crack is most evasive in that the localization of the radicals produced does not lead to significant sensitivity in the spectrometer cavity. Thus, the technique has proved to be most useful for ubiquitous production of radicals throughout the sample.

From a conceptual viewpoint the primary theoretical problem yet to be solved is the stress transfer mechanism in polymer solids. As noted earlier, polymers have statistical structures when in the glassy state and a rather broad spectrum of order-disorder when in the crystalline state. Detailed analysis of stress transfer through a glassy structure requires comprehensive analysis of chain conformation in the (nonequilibrium) glass which in turn requires an understanding of both the intramolecular and intermolecular energetics.

Crystalline polymers appear to be the most studied by ESR techniques. The model which seems to emerge from these results is, in fact, a variant of a model proposed over twenty years ago by Cumberbirch and associates (Shirley Institute Memoirs) to explain the tenacity of wet rayon monofilaments. Briefly, Cumberbirch, *et al.* propose a fringe-micelle structure in which the fringe regions, swollen by water, are assumed to obey rubber elasticity theory. These fringe regions are, of course, the more accessible (to water), more disordered, regions of the semicrystalline structure.

A statistical distribution of connector chain lengths, which depends on both the micelle spacing and the distribution of chain lengths (degree of polymerization), connects the micelles. As stress is applied to the sample the average spacing between micelles changes and results in nonuniform strain among the connector chains. Cumberbirch then invokes a taut chain failure criterion and calculates the average strain at which the unbroken chains can no longer accept the extra stress imposed on them by the rupture of the next taut chain. The failure process described by Cumberbirch is in essence the model which seems to be in reasonable agreement with the ESR studies of failure in crystalline polymers.

While the fringe-micelle model for crystalline polymers has not been fashionable for some time, it may have some utility in modeling stress transfer and failure mechanisms. In any event, a fringe micelle model is a primitive form of more general composites models which attempt to model the behavior of crystalline polymers using the same techniques as for filled systems or fiber reinforced plastics. The ESR studies may serve to provide valuable insight into the validity of such models for

crystalline polymers particularly in regard to the manner in which stress is shared or distributed in the more disordered regions.

Applications of linear elastic fracture mechanics (primarily) to the brittle fracture of solid polymers is discussed by Professor Williams. For those not versed in the theory of fracture mechanics, this paper should serve as an excellent introduction to the subject. The basic theory is developed and several variants are then introduced to deal with weak time dependence in solid polymers. Previously unpublished calculations on failure times and craze growth are presented. Within the framework of brittle fracture mechanics and testing this paper provides for a systematic approach to the failure of engineering plastics.

Several cautions are, however, in order. Polymers are notorious for their time dependent behavior. Slow but persistent relaxation processes can result in glass transition type behavior (under stress) at temperatures well below the commonly quoted dilatometric or DTA glass transition temperature. Under such a condition the polymer is ductile, not brittle. Thus, the question of a brittle-ductile transition arises, a subject which this writer has discussed on occasion. It is then necessary to compare the propensity of a sample to fail by brittle crack propagation versus its tendency to fail (in service) by excessive creep. The use of linear elastic fracture mechanics addresses the first failure mode and not the second. If the brittle-ductile transition is kinetic in origin then at some stress a time always exists at which large strains will develop, provided that brittle failure does not intervene.

An additional complication for glassy polymers is their spontaneous aging for many years following vitrification. Linear elastic fracture mechanics can only treat the crack propagation parameters that currently prevail in the test specimens.

For the reasons cited, it is prudent to evaluate plastics for long term stress-supporting applications using linear elastic fracture mechanics in conjunction with other rheological and thermophysical data, particularly regarding long time behavior, aging phenomena, and failure modes.

Failure in multiphase polymers and polymer composites (non-fibrous) is reviewed by Professor Bucknall. Several examples are presented in which the effect of adding a dispersed second phase to a polymer can be either beneficial or deleterious to stress, strain, or work to break. It is shown that two basic modes of local plastic deformation may be operative, namely crazing and shear band formation. By studying the sample dilatation versus strain in uniaxial tension creep tests, Bucknall is able to determine the operative mechanism in each system. Fracture mechanics is used to evaluate the toughness parameters of the various systems.

It is noted that attempts to apply composites theory to the materials investigated have not been entirely successful. While upper and lower bounds on, *e. g.*, moduli can be established there is little quantitative prediction of the impact strength or fracture toughness parameters of the composites. Hence, the systems cannot be considered as optimized, for example, with regard to impact strength versus particle size, shape, or distribution or matrix-particle adhesion. The complexity is, of course, due to the statistical structure of the dispersed phase and the resultant uncertainties in the calculations of *local* stress fields, which in turn imply uncertainty in the local mode of yielding or rate of yielding.

Conceptually, the problems associated with the optimization of specific mechanical properties by variations of structure and morphology are the same in rubber-filled systems, glass-bead filled systems and semicrystalline polymers. When the fracture properties are singled out, our understanding of the relationships between macroscopic failure and local failure is hampered by the limited knowledge of stress transfer in statistically nonhomogeneous structures. The increased use of composites theory and micromechanics to address these problems would appear to be appropriate.

Professors Andrews, Williams, and Bucknall have summarized the current status of the molecular, phenomenological, and materials aspects of failure in polymers, respectively. Any future developments in the linkage among these three approaches will, of necessity, serve to enhance each of them with the knowledge of the others.

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