27 Advances in Polymer Science

Fortschritte der Hochpolymeren-Forschung

"Failure in Polymers: Molecular & Phenomenological Aspects"

Cantow, H.-J., Dall' Asta, G., et al.

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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 triumpf 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 mechanical 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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Molecular Fracture in Polymers

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Molecular Fracture in Polymers

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1. Approaches to Fracture

The subject of fracture is of both practical and scientific interest. The propensity of a material to fracture sets limits both to engineering design and to the service life of engineering components and structures. Questions of safety, as well as convenience, are deeply involved.

At the same time the phenomenon of fracture reflects, in one way or another, the ultimate limit of deformation in a solid. It thus involves fundamental physical properties of the material such as its inter-atomic bonding, its surface energy and its crystal structure. It also involves crystallographic processes such as slip, stress induced phase transformations and twinning, whilst in molecular solids such as polymers other processes such as molecular relaxation behaviour may predominate. Fracture is clearly of great scientific interest and has attracted the attention of chemists and solid state physicists as well as engineers.

It is not surprising therefore that the subject has, historically, been approached from a variety of different viewpoints. In this introductory section we review briefly these various 'approaches to fracture' and point out the methods by which they can be co-ordinated and, where necessary, reconciled with one another.

1.1. Continuum Mechanics

This approach is the most useful for engineering purposes since it expresses fracture events in terms of equations containing measurable parameters such as stress, strain and linear dimensions. It treats a body as a mechanical continuum rather than an assembly of atoms or molecules. However, our discussion can begin with the atomic assembly as the following argument will show. If a solid is subjected to a uniform tensile stress, its interatomic bonds will deform until the forces of atomic cohesion balance the applied forces. Interatomic potential energies have the form shown in Fig. 1 and consequently the interatomic force, which is the differential of energy with respect to linear separation, must pass through a maximum value at the point of inflection, P in Fig. 1.

This maximum load-bearing capacity of the atomic bond can be expressed[1] as a breaking stress for the bond, thus,

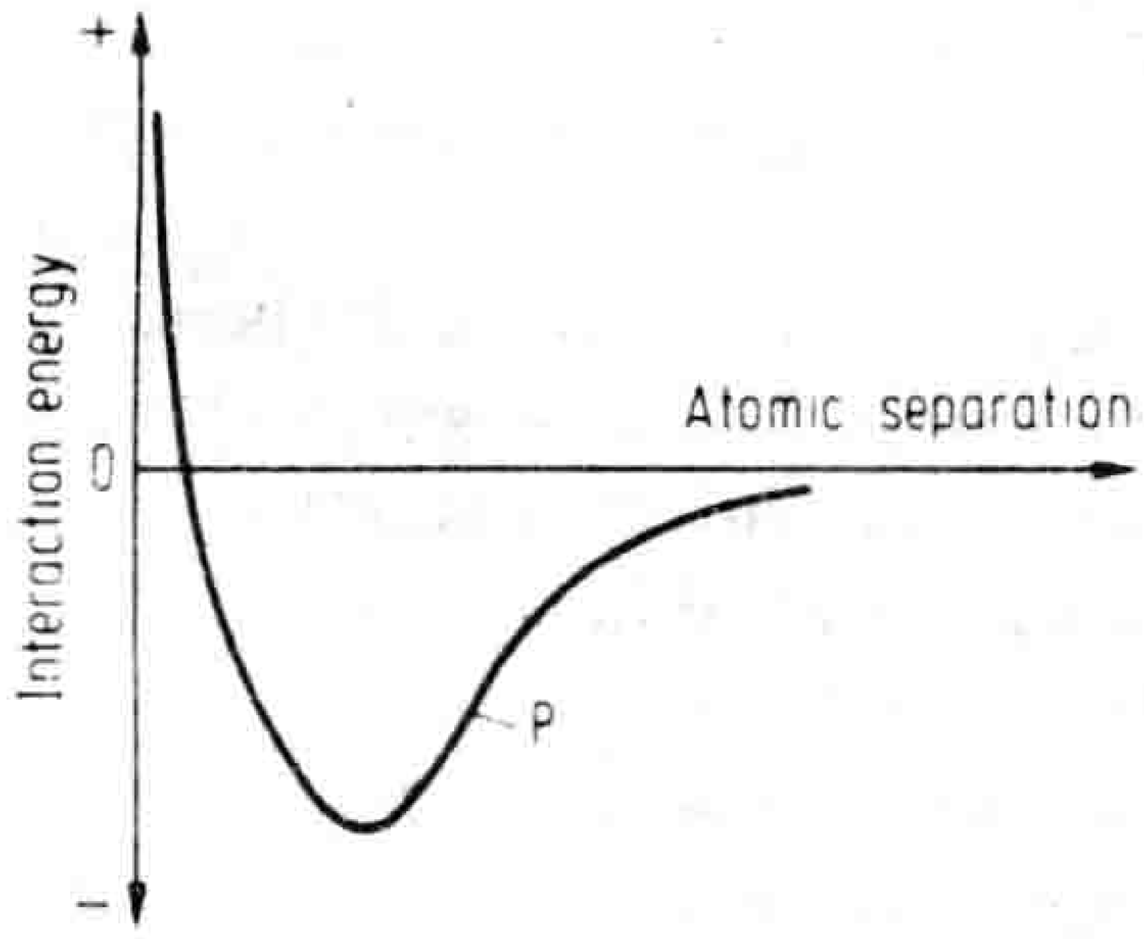

Fig. 1. Interatomic potential energy (schematic)

$$\sigma_m \simeq E\epsilon_m \tag{1}$$

where E is the Young's modulus of the solid, and ϵ_m is the strain at which σ_m is achieved. Since most laws of force between atoms joined by primary bonds give an ϵ_m of 0.1 to 0.2, the bond fracture stress can be written

$$\sigma_m = \alpha E \tag{2}$$

$$0.1 < \alpha < 0.2$$

The simplest continuum approach to fracture is to ascribe to the continuous solid the strength of its individual atomic bonds. Thus,

$$\sigma_f = \sigma_m = \alpha E \tag{3}$$

where σ_f is the macroscopic fracture stress.

It is well known that this "theoretical strength" is seldom, if ever, achieved by solids, although freshly drawn glass fibres and certain whisker crystals do appear to exhibit tensile strengths approaching the theoretical limit.

Bulk solids, generally, exhibit α values in Eq. (3) between 10^{-2} and 10^{-4}, that is one to three orders of magnitude smaller than expected, and this is ascribable to flaws, cracks and imperfections in the body which concentrate stress[2)].

The idea that the strength of bulk solids is controlled by flaws was advanced by Griffith[3)] in 1921 and has led to the development of a much more sophisticated continuum approach to fracture, known as fracture mechanics. Fracture mechanics is concerned always with the conditions for the propagation of an existing crack, and it is important to bear this in mind when comparing different theories of fracture. Griffith's ideas are well known and do not need to be elaborated here. There are some aspects of his theory which are relevant to the present discussion, however. Griffith's equation for the fracture stress of an elastic material is (for plane stress),

$$\sigma_f = \sqrt{\frac{2ES}{\pi c}} \tag{4}$$

where S is the surface energy of the solid and c the length of the largest pre-existent crack. For this equation to give the correct limit as $c \rightarrow 0$, the term c should be replaced by $(c + d)$ where d is the interatomic spacing. Furthermore, the surface energy S needs to be carefully defined. Strictly, it is half the energy required to fracture unit area of inter-atomic bonds across the fracture plane, this plane being created by propagation of the pre-existent flaw.

The important point about Griffith's theory is that is *does* contain the bond fracture energy, or bond strength, explicitly in the term S. This distinguishes the theory from all subsequent theories of fracture mechanics with the exception of the "generalized theory" recently proposed by Andrews[4)]. Thus although Griffith's is a continuum theory it does relate directly to atomistic parameters.

Unfortunately the theory is derived for purely elastic solids and cannot handle the inelastic deformations (and thus energy losses) which normally predominate in the vicinity of a crack tip nor the time and temperature dependence commonly found in fracture. As a result Griffith's equation predicts fracture stresses much lower than are normally observed, even in brittle materials.

Two methods have been adopted to overcome this problem. In the first, due to Orowan[5)] and others[6)], the term S is generalized to include dissipative energy contributions which are thus, somewhat arbitrarily, assigned to the new crack surfaces although they actually occur over a volume distribution around the crack tip and even throughout the stressed body. In this paper we shall use the expression $\mathcal{T}$ to represent this modified "surface energy" and we shall call it the "surface work".

The difficulty here is that $\mathcal{T}$ is no longer related in a discernable manner to the physical properties of the solid and must be treated as an empirical quantity which, hopefully, is constant for a given material. As it happens, $\mathcal{T}$ is found to vary with such things as rate, temperature and sheet thickness.

The second approach, due to Irwin[7)], is to characterise the stress field surrounding a crack in a stressed body by a stress-field parameter K (the "stress intensity factor"). Fracture is then supposed to occur when K achieves a critical value K_c. Although, like Griffith's equation, this formulation of fracture mechanics is based on the assumptions of linear elasticity, it is found to work quite effectively provided that inelastic deformations are limited to a small zone around the crack tip. Like $\mathcal{T}$, however, the critical parameter K_c remains an empirical quantity; it cannot be predicted or related explicitly to the physical properties of the solid. Like $\mathcal{T}$, K_c is time and temperature dependent.

Thus, whilst the science of fracture mechanics has flourished as a means of defining fracture properties for engineering purposes, it remains basically empirical; the critical parameters (like $\mathcal{T}$, K_c, J_c, δ_c) cannot be predicted from, or related to, the physical properties of the solid in question.

This situation has been resolved, at least in part, by a recent generalized theory of fracture mechanics[4)] which gives,

$$\mathcal{T} = S\Phi(\dot{c}, T, \epsilon_0) \tag{5}$$

Here $\mathcal{T}$ is again the surface work, S is the surface energy as previously defined and Φ is the "loss function" dependent on crack speed, temperature and the strain, ϵ_0, applied to the specimen. The theory gives Φ explicitly in terms of the energy density distribution in the specimen and the plastic or visco-elastic hysteresis of the material.

In principle, then, the surface work $\mathcal{T}$, which determines the fracture stress of the body can be calculated from the physical properties of the material. In practice this is not easy, since the energy density distribution can only be calculated exactly for linear elastic solids, for which $\Phi \to 1$ and Eq. (5) reverts to the Griffith theory. However, Eq. (5) has been found correct for a series of highly extensible materials in which the energy density distribution was measured experimentally[8)].

The generalized theory therefore restores the explicit link between a continuum mechanics approach to fracture, which is of such great value in engineering design and practice, and the atomistic view which concerns us most in this review. This link has been lost since Griffith's theory was found to be inadequate for most real materials, but is now reinstated by means of the same parameter employed by Griffith, namely the surface energy S.

1.2. The Nature of the Surface Energy

We now examine more closely the significance of the term S. As previously noted, this is not the quantity normally referred to as surface energy and which controls *e.g.* the contact angles of liquids on solid surface. The latter (we will denote it γ_s, or γ_{sv} if the solid is in contact with a vapour phase as is usually the case) only corresponds to S in rather unusual circumstances, such as ultra-clean metal surfaces in vacuum. For polymeric solids, γ_s reflects only the weak secondary bonding that exists between molecules, whereas S (the energy to break unit area of bonds across a fracture plane) normally contains major contributions from primary bond rupture.

For metals and ionic solids, in which atoms interact only by omni-directional primary bonds, it is clear that S will be the fracture energy of such bonds normalised to unit area. For co-valently bonded solids, like diamond, the secondary bonding energies are negligible with respect to the primary bond strengths so that S will be given directly by the latter – again normalised to unit area.

Molecular solids like polymers present greater problems since the creation of surfaces may involve the severence of primary (intra-molecular) or secondary (inter-molecular) bonds, or, more likely, both simultaneously. In thermoplastics it is possible to envisage molecular "pull-out" in which no molecules are broken but are simply separated from one another against the frictional secondary bonding forces. In network polymers, of course, surfaces can only be created by breaking primary bonds, but these may be relatively widely spaced. Crystalline thermoplastics and indeed amorphous polymers with very long molecules may behave (in this respect) more like network polymers because crystals or entanglements act as effective cross-links.

A theory due to Lake and Thomas[9)] appears to provide a satisfactory account of the origin of the parameter S in cross-linked systems. (In the literature the symbols $T_0 \equiv 2S$ and $\mathcal{T}_0 \equiv S$, are used, indicating minimum or threshold "tearing energy" referred respectively to unit area of fracture plane *i.e.* two surfaces, and unit area of fracture surface).

Lake and Thomas supposed that no primary bond in a cross-linked network can fracture unless all the bonds in that particular network chain (*i.e.* between adjacent cross-links) are stressed to breaking point. Thus, if there are $\bar{n}$ inter-atomic bonds between cross-links (on average) the minimum energy to cause *one* bond to fracture is not the dissociation energy of one bond but n times that energy. Their prediction takes the form

$$S = \bar{L} N \bar{n} \, U/2 \qquad (6)$$

where $\bar{L}$ is the mean displacement length between cross-links (*i.e.* the distance between cross-links in the unstrained state), N is the number of network chains per unit volume and U is the dissociation energy of a single bond.

The theory predicts S values in the range 10–20 Jm^{-2} for normal cross-linked elastomers, depending of course on cross-link density. This compares favourably with minimum tearing energies measured experimentally by fatigue-limit observations[10)] and other special techniques and which lie in the range 20–50 Jm^{-2}. A modified form of the theory was used by King[11)] to calculate S for epoxy resin networks and again agreement with experiment was obtained within a factor of two. These experimental measurements of S are possible for cross-linked elastomer networks only because, at low rates of crack propagation and elevated temperatures, visco-elastic losses can be reduced to zero, giving $\Phi \to 1$.

A different approach to the determination of S was adopted by Andrews and Fukahori[8)] who treated S as the unknown in Eq. (5) and found values of 65 Jm^{-2} for SBR and EPDM rubbers and 100 to 200 Jm^{-2} for polyethylene and plasticized PVC. The latter represent the first determinations of S for non cross-linked polymers.

The values cited are, of course, of the order of 10^3 times γ_{sv} for polymeric solids, emphasizing the difference between S and γ. They are also up to 100 times the surface energy values to be expected from "high surface energy" solids such as clean metals and oxides (< 0.5 Jm^{-2}). It is clearly necessary to invoke the mechanism of Lake and Thomas to explain these high S values in polymeric materials.

Under some circumstances it is possible to observe very low S values for polymer solids, namely when the energy to fracture chemical bonds is provided by chemical reaction. An excellent example of this is the ozone cracking of unsaturated hydrocarbon elastomers where crack propagation occurs at threshold values of $\mathscr{T}$ as low as 0.05 Jm^{-2}[12)]. Under such low stresses the loss function of Eq. (5) is effectively unity and $\mathscr{T} \sim S$. Then S is probably nothing more than the surface energy of the (liquid) degraded rubber at the tip of the crack.

Low values have also been recorded[13)] in the solvent stress-crazing of glassy plastics, where in appropriate circumstances $S \sim 0.1$ Jm^{-2}. In this case, however, the surface energy in question is that of voids and cavities in the craze.

To summarize, therefore, we conclude that the fracture resistance of solids as reflected in the parameter $\mathscr{T}$, is controlled by

(i) the mechanical energy losses which determine Φ and

(ii) the energy required to sever interatomic bonds across the fracture plane.

In cross-linked polymers, crystalline polymers and high molecular weight glasses, the bond fracture energy per area, S, is dominated by the strength of co-valent intramolecular bonds. The only exception is where the energy to rupture these bonds is supplied by extraneous chemical means rather than by mechanical stress. Although a higher concentration of cross-links, tie points or entanglements increases the number of co-valent bonds to be broken in unit area, this effect is more than offset by the Lake-Thomas effect which requires an entire network chain to be energised to break for each bond that actually ruptures. Thus, paradoxically, the fewer the cross-links, the higher does S become until, of course, the contribution to S of secondary bonds begins to predominate when S will fall again.

Further studies of the significance of S in polymer fracture will certainly be carried out in future research. The main purpose of the forgoing discussion, however, is to emphasize that molecular fracture is not a scientific curiosity but plays a major role in determining the resistance of polymer solids to failure. Hopefully,