

## POLYMERS AND OTHER COMPOSITES

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**Abstract**—The structure-morphology-property relationship of such classical solids as metals, oxides and ceramics, and of organic crystals has been quite successfully explored, but our corresponding knowledge of polymeric materials is still very incomplete. The work in progress today considers the very different magnitudes of domains and numbers of dislocations in these two classes of materials, the differences in the interfaces, and the much greater extensibility of the polymeric molecule. Most progress has been made so far in the field of highly crystalline polymers, of block co-polymers, and of polymers filled or laminated with reinforcing or rubberizing agents. Here again, a great deal of work has centered on the role of chain mobility in the dissipation of energy, the special part played by the interphase as locus of flaw formation or stoppage, and on the very large structure changes during work hardening.

The most useful approach starts from the known mechanics of dispersed systems and composites, adapting them to the special morphologies of polymers, particularly of the partly crystalline-amorphous variety. The moduli are found to follow the established theory of inhomogeneous elastic solids rather well, and so do solubility, density, heat capacity and optical behavior. Their capacity for absorbing energy depends greatly on temperature and rate of deformation, which in turn depend on the cohesive energy based on molecular chemistry. The greatest difficulties arise in the understanding of the effects of processing history and from the extensive deformation, delayed internal elasticity, and miscibility and phase boundary defects typical for long chain materials. Studying failure behavior is unduly complicated by our lack of understanding of ultimate properties in small domains ahead of propagating cracks. Block polymers are particularly good subjects for learning more about domain properties.

Synthetic linear macromolecules, in brief "Polymers", have had a phenomenal development during the last 30-40 yr, technologically as well as scientifically. Their use as fibers, films, elastomers, foams, adhesives, coatings, containers, and/or most disposable items of modern life, exceeds now the total volume of metals. However, when compared with metals, and even with natural macromolecular materials like those based on cellulose and silicates, their use for structural or load bearing applications is relatively modest.<sup>1</sup> Design engineers are reluctant to employ polymers because, relative to conventional materials, synthetic polymers have such drawbacks as: low moduli, low temperature resistance, viscoelastic rate dependence, creep, aging, and sudden failure through stress and solvent cracking. The use of polymers as a class suffers sometimes also under the variability of their properties which are sensitive functions of the manufacturing methods, and of their thermal and mechanical history in general. Yet, the very strength and wide utility of wood, the successful uses of synthetic polymers in laminates where lightweight, corrosion resistance and toughness are required, and progress in the past decade with filled and toughened polymers, poly-blends, and block-copolymers, prove the potential value of synthetics as engineering materials.

The most typical polymeric properties are an inevitable consequence of the tendency of long chain molecules to pack very irregularly when freezing, undercooling, or precipitating. Thus, solid polymeric materials are always thermodynamically unstable multiphase mixtures of intermingling crystalline, glassy or rubbery domains with corresponding local density variations, flaws, dislocations, and grain boundaries, which cause them to be at least as, if not more, inhomogeneous than metals and ceramics, and more vulnerable than the latter to aging and rupture processes under attack of vibrations, thermal and mechanical shock, and surface damage by solvents and oxygen. Figures 1 and 2 illustrate two examples of aging and failure phenomena in polymers, the first showing the effect of annealing on creep,<sup>2</sup> and the second the sudden

rupture of an elastomer under constant load during stress relaxation,<sup>3</sup> see also Fig. 27.

On the other hand, Figs. 3(a,b) show the great improvement of, e.g. polyethylene terephthalate on crystallization, esp. with respect to toughness and ductility.<sup>4</sup> Table 1, a comparison of the moduli and strength of some polymers with metals provides further evidence that not only may polymers measure up to them with respect to strength, but that in particular their strength-to-weight ratios can be superior,<sup>5</sup> a great advantage for many constructions and in all automotive and aircraft applications. Including an almost unlimited number of further examples, we may deduce that the properties of polymers are as much affected by molecular organization as by chemistry. In particular, isotropically solidified assemblies of chain molecules of low order of molecular organization ("amorphous") are indeed limited in their load bearing capacities because one engages there only the intermolecular forces. In partly ordered, partly disordered, polymers with crystalline domains interspersed in vitreous or rubbery domains, or vice versa, the strength is much improved because, in the former, centers of plastic deformation are introduced, and

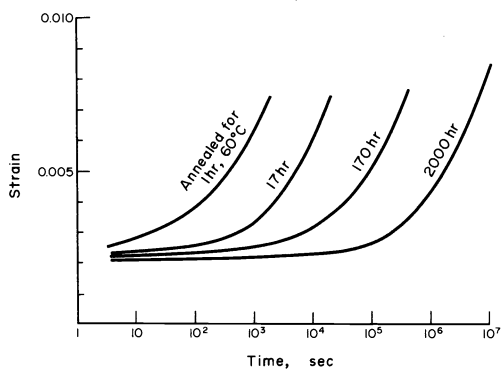


Fig. 1. Creep data (PVC), showing a strong dependence on thermal history. The annealing process is specified for each curve.<sup>2</sup>

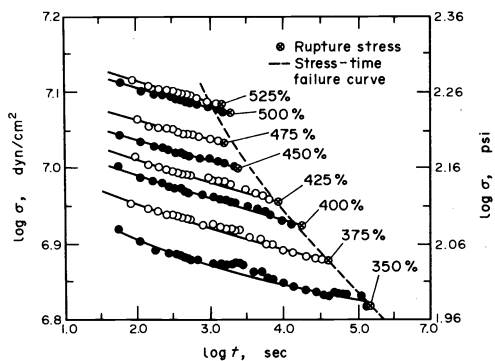
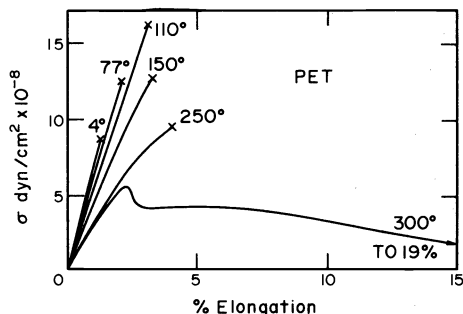
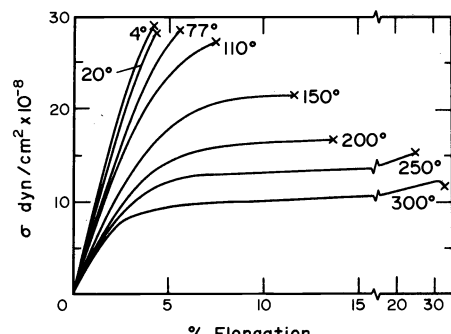


Fig. 2. Stress-relaxation curves which terminate in rupture. Data for SBR-II at 2°C.<sup>3</sup>



(a) Melt cast, amorphous



(b) Oriented, heat set

Fig. 3. Stress-strain behavior of Mylar A in tension at various temperatures.<sup>4</sup>

in the latter moduli and dissipation are increased. Whenever macromolecules are oriented as fibrils parallel to the stress and strain axes, the polymer becomes extremely strong, depending on how well ordered and densely packed the chains are per cross-section. The toughness of polymeric materials arises from the presence of less ordered domains of extendable chains between the crystallites, capable of work hardening and of dissipating substantial amounts of energy while crystallizing during straining. The main topic of my presentation, therefore, will be that polymers in the solid state are much more heterogeneous, much more flawed, but also much more extendable and orientable than other materials and therefore more capable of developing maximal strength in specific directions. Since the combination of strength and toughness depends on the simultaneous presence of anisotropic and isotropic orientable domains, they are, on a microscale, of analogous organization as man-made laminates or composites. This entails the expectation that, if we could learn to influence the molecular organization in a given specimen in an optimal functional fashion, similar to the specific designs of laminates, we could produce very superior molecular composites without the drawbacks of the man-made ones. Vice versa, the mechanics of composites should help to develop the needed micromechanics for polymer materials.<sup>6</sup>

Towards these ends we have to understand the details of molecular organization whose features are responsible for the peculiarities of polymers as structural materials. Figure 4, borrowed from Pechhold,<sup>7</sup> shows the principal molecular forms, referring in particular to the ideal and the faulted chain packing, especially to kinks and segmental rotation as principal means for the development and propagation of dislocations in solid polymers, and also changes in molecular packing from dense parallel bundles to increasingly disordered states and (interpenetrating) random coil molecules. Figure 5 shows the reality of linear and lamellar molecular organization in the case of an extruded polyethylene film.<sup>8</sup> The micrograph shows clearly the extended molecules in the stress direction (upper left to lower right) which became the nucleating agents for the perpendicular folded lamellae which form the spherulites of crystalline polymers. The interaction of linear and folded domains is shown schematically on Fig. 6.<sup>9</sup> Altogether, Fig. 5 gives a good impression of the heterogeneous structure of most solid polymers. Figure 7, borrowed from Hosemann,<sup>10</sup>

Table 1. Properties of oriented polymeric chain structures and related engineering materials

Material	$E_{11} \times 10^{-6}$ , (psi)	$E_{22} \times 10^{-6}$ , (psi)	$\bar{E}_{iso} \times 10^{-6}$ , (psi)	Tensile strength, (ksi)	Density, (lb/in <sup>3</sup> )
Steels and iron (case and alloy)			28-30	13-300	0.25-0.29
Titanium			19	60-240	0.16
Poly(vinyl alcohol)	36.2	1.54	14.4	~100	0.05
Polyethylene	34	0.7	13.6	~100	0.05
Boron/epoxy	30	2.7	11.89	83	0.07
Aluminum			10	22-90	0.10
Polytetrafluoroethylene	22.2				0.05
HTS-graphite/epoxy	21	1.7	10	62	0.05
Cellulose I	18.5		7.6	50	0.05
E-glass/epoxy	5.6	1.2	2.85	47	0.06
Polypropylene	6.0	0.42	2.5		0.05
Poly(ethylene oxide)	1.42	0.56	0.88		0.05

See Ref. (5).

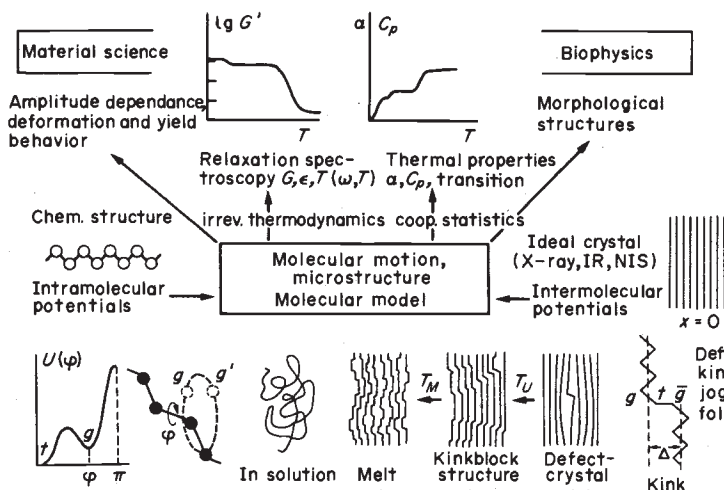


Fig. 4. Scheme of molecular approach to micro-structure and molecular motion in polymers, and their physical properties.<sup>7</sup>

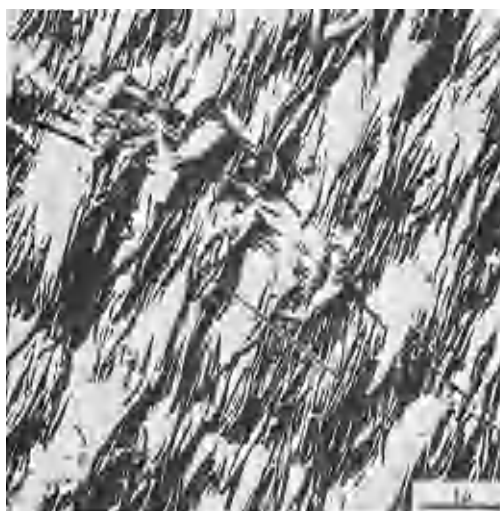


Fig. 5. Surface of blown film of polyoxymethylene showing the nucleating fibrils aligned in the extrusion direction with twisted bundles of lamellae oriented normal to the fibrils. Electron micrograph.<sup>8</sup>

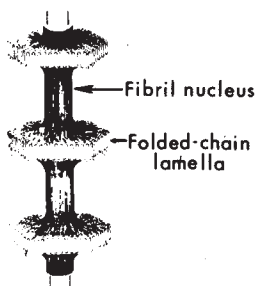


Fig. 6. Schematic representation of linear and folded domains, the so-called "shish kebab" structure.<sup>9</sup>

summarises what we know about the internal molecular organisation of crystalline polymers, pointing out the flaws, shear planes, tie chains, and boundaries of crystal growth, typical for these crystal habits. This same figure also indicates the unlimited variability of the

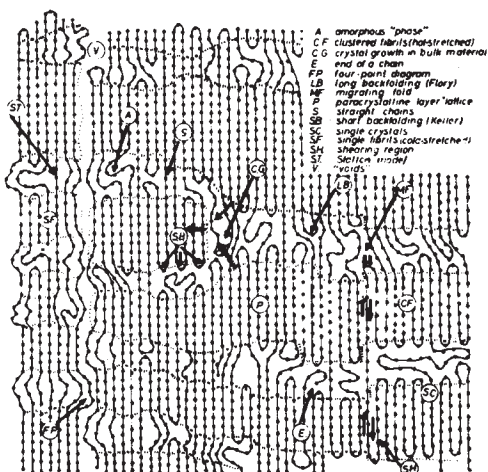


Fig. 7. Model of linear polyethylene domains.<sup>10</sup>

molecular organisation, makes understandable the dependence on the method of preparation, is indicative of the thermodynamic instability relative to the well ordered linear crystals, but also points out the potential for structural change in every real solid polymer.

Figure 8 extends the concept of heterogeneity and domain character to polymeric glasses and emphasizes

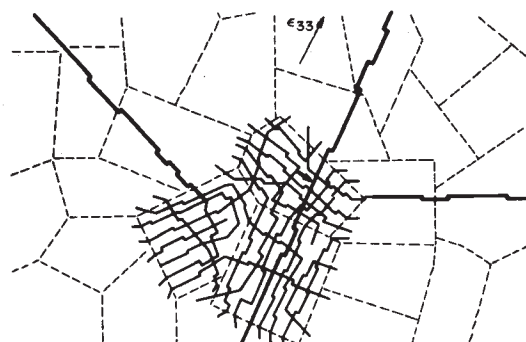


Fig. 8. Model of an amorphous high polymer. The heavy lines indicate molecules which—by chance—possess an almost extended conformation over a length of several molecular domains.<sup>11</sup>

again the presence of tie chains which act as mechanical messengers, or mechanical links, between the domains.<sup>11</sup> In this context, one should remember that the change in entropy per macromolecular segment during solidification is comparable to, but less than, that of a small molecule. The entropy change for the whole macromolecule is of course extremely high. Though, therefore, the driving force for, and rate of, local packing is about the same for monomer or between monomeric units within chains, the very large entropy loss for the macromolecule and the rapidly rising internal friction during solidification make it most difficult for the macromolecular as a whole to reach a highly linear organisation. Thus, even polymeric glasses possess domains and a heterogeneity greater than that due to thermal fluctuations.

The creation of a higher degree of order, and reduction of the amorphous zones during annealing, leads to volume contraction and to a diminishing of the internal mobility, and places an extra burden on the tie chains. What happens to the latter is sketched in Fig. 9, which

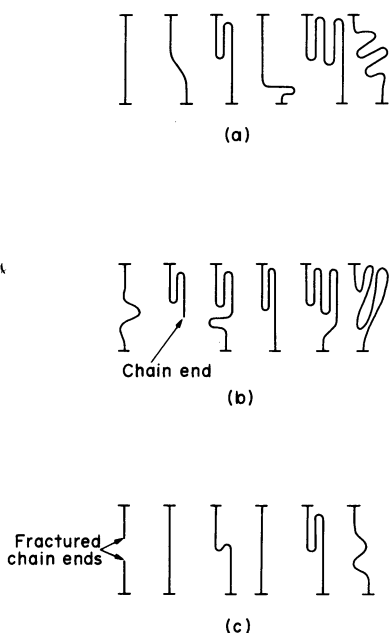


Fig. 9. Schematic representation of irreversible type changes created in the tie chain distribution under slack and tension annealing: (a) unstressed control; (b) unstressed slack-annealed sample; (c) unstressed tension-annealed sample.<sup>12</sup>

demonstrates the pulling-back and rupturing of tie chains during stress or strain relaxations<sup>12</sup> with time, especially when thermally accelerated. The increasing number of flaws and decreasing number of load bearing tie chains explains the sudden failure, or stress corrosion after a time (see Fig. 2).

Figures 10 and 11 demonstrate the process of chain alignment and crystallation under stress, perhaps the most crucial feature of macromolecular reorganisation when undergoing large elongations. This ability is inherent in all linear polymeric materials, and becomes operative when the free volume increases above a critical average value during thermal expansion or uniaxial extension. The process itself consists of an increasing straightening of individual chains, accommodating themselves to the imposed strain by their alignment and packing. This is shown by a steep upswing of the stress-strain curve at higher elongations and accompanying increases in strain birefringence, i.e. by the workhardening, or orientation hardening, which is so typical of crystallisable polymers above the glass transition.<sup>13</sup> Figure 10 gives the stress-strain curve of an elastomer as a reciprocal Mooney-Rivlin plot.<sup>14</sup> The straight portion shows the conforming to Gaussian behavior, including the  $C_2$ -term.

The first upswing at *P* is due to incipient crystallization caused by tie chains, the following drop at *Q* indicates stress relaxation due to minor crystallization, and the final steep rise at *R* shows the modulus increase due to orientation hardening.

Figure 11, due to Peterlin<sup>15</sup> summarizes diagrammatically

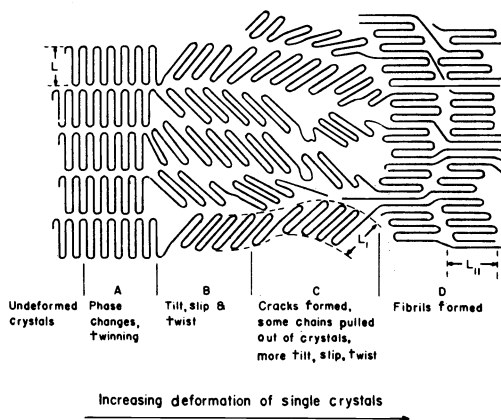


Fig. 11. Suggested model for fibril formation by gradual chain tilting, slip, and breaking off blocks of folded chains.<sup>15</sup>

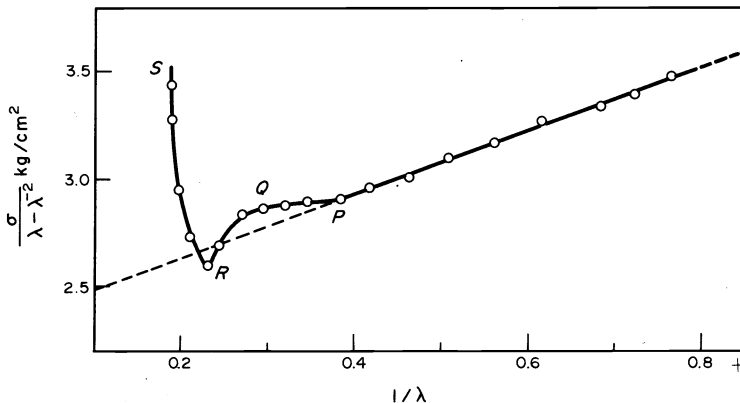


Fig. 10. Example of Mooney-Rivlin plot demonstrating the influence of the finite extensibility of network chains and stress crystallization. Data for natural rubber at 0°C.<sup>14</sup>

his microscopic observations during cold flow. On the left are the original folded chains of a spherulitic structure which, on being stressed, begin to tilt into the stress axis, then melt partially under the influence of stress induced free volume increase (Poisson) and of plastic and viscous friction, and finally re-align, under retention of some folds, along the stress axis. This means that the *c*-axes of the crystal has been tilted 90°. An actual temperature rise can be measured in the necking zone and, vice versa, locally applied heat enhances necking. Cold drawing is thus seen to be a process by which stress-parallel orientation and the strength of fibers is enhanced. Super strong fibres like those reported on by Porter<sup>16</sup> are produced by further cold drawing of predrawn fibers. Porter estimates that his best fibers at over 80% crystallinity are approximately 20% fully aligned which indicates the further improvement of strength that can be expected.

Figures 7 and 8 show also the existence of voids the formation of which is depicted in greater detail in Fig. 12.<sup>17</sup> The onset of void formation is usually quite sudden and occurs at critical values of stresses or strains described by failure criteria, see for instance the work of Kambour<sup>18</sup> and by Sternstein.<sup>19</sup> Craze usually antecedes failure and in many cases is a potent stress relief mechanism in that the creation of internal surfaces as well as the spinning out of workhardening fibrils between the opening craze walls consumes great amounts of energy. Crazes may be assumed to occur at sites of widely scattered weak spots and are recognised by the so-called stress whitening which is the result of light reflection and refraction from internal surfaces. Initial crazes are so small that their formation can be followed by low angle x-ray scattering which recently has been used as a tool to determine the crazing tendency of polymers as a function of their composition, state of annealing, or reinforcement by small inclusions.<sup>17</sup> Indeed, much of the reinforcing or toughening actions of multiphase polymers can be traced to an enhancement of crazing within the interphase between particles and matrix.<sup>20</sup>

Most of the recently developed polymeric materials, discussed further below, were engineered with the above model of craze development and crack propagation in mind. The development, of fiber reinforced, or laminated resins, however, began from reverse considerations, i.e. from the observation that, when embedded in a polymeric matrix, loadbearing, high modulus, elements developed

fewer cracks which became less catastrophic, or did not propagate to the next load bearing element. The second observation is readily explained by the ability of the polymer, see again Fig. 11, to undergo large viscoelastic and/or plastic elongations, to dissipate elastic energy and to workharden at the apex of the crack when the latter transgresses from the fiber into the matrix.<sup>20</sup> This response mechanism of linear chain polymers in tensile fields, to sustain large deformations, to become stiffer with strain rate, and at the same time more plastic with increasing orientation, is the principal cause for their fracture toughness.<sup>21</sup>

The increased ductility of the hard loadbearing, phase is more difficult to understand. Most likely is it not the difference in Poisson ratios, or the cavitation resistance of the matrix, but that the adsorbed interphase acts like an adhering crossply whose resistance to rupture in shear delays the formation and growth of surface cracks on the hard phase until the yield value of the latter is reached. Thus, the mechanical interrelation between the heterophase structure of polymers and of man made composites has also a fracture mechanical basis.

Similarly, the principles of mechanics, suitably modified as micromechanics so as to apply to polymeric as well as man-made laminates alike, permits the application of the same models, formalisms, and mathematics to both systems.<sup>5,6</sup> Figures 13 and 14 show the well developed micromechanics of composites applied to the molecular composite structure of spherulites,<sup>6,22</sup> and some of the relevant equations for the required number of moduli. Many polymeric materials can be treated as composites of specific structure, and fall between the lower and upper bounds of the moduli for a parallel and an in-series lay-up.<sup>5</sup> Figure 15 shows that calculations and experimental data agree well for a number of composites and polymeric materials.<sup>5</sup>

In this context, one has to mention block copolymers which we now understand sufficiently well to be able to obtain the dispersed phase in spherical, filamentous, or lamellar form, invert phases according to the component ratio and prepare dispersions of predetermined particle size according to the molecular weight ratios of the components. Block copolymers show the two or three mechanical loss maxima, typical for their sections, exhibit extensive stress-strain hysteresis, and extensive crazing which is frequently reversible, at critical stresses.<sup>23,24,25</sup>

From our understanding, then, of polymeric morphology and domain structure, its bearing on mechanical properties, on permeability, electrical resistivity, flammability, chemical resistance, etc. and from what we know about the micromechanics of composites—what is being done today, and what may we expect can be done in the future, to improve the value of polymers as structural materials? More specifically, what can we do to reduce creep, stress relaxation, stress corrosion, aging etc., or to control the processing variables? Obviously, we must learn to manipulate the molecular organisation in pure and multicomponent polymers and in the matrices around loadbearing elements, understand to align the molecules in such a way that they offer the densest packing in cross sections perpendicular to the principal stress, and learn to predict elastic limits, plastic deformation, extent of work hardening, the failure pattern, and to increase the reliability of polymers in service.

Much progress is being made to answer all these questions without that one could as yet integrate the results into a coherent system, to some extent because of lack of joint planning. Among the many efforts, theoretical work is being

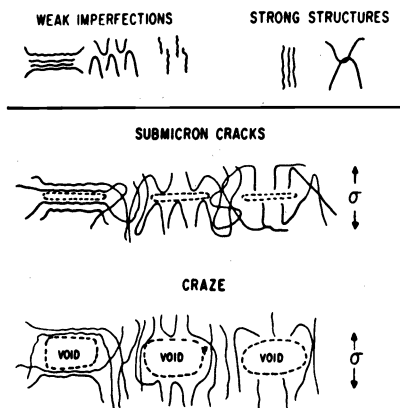


Fig. 12. Postulated weak imperfections and strong structures in glassy polymers along with a possible mechanism for the initial void structure observed by SAXS during the crazing process.<sup>17</sup>

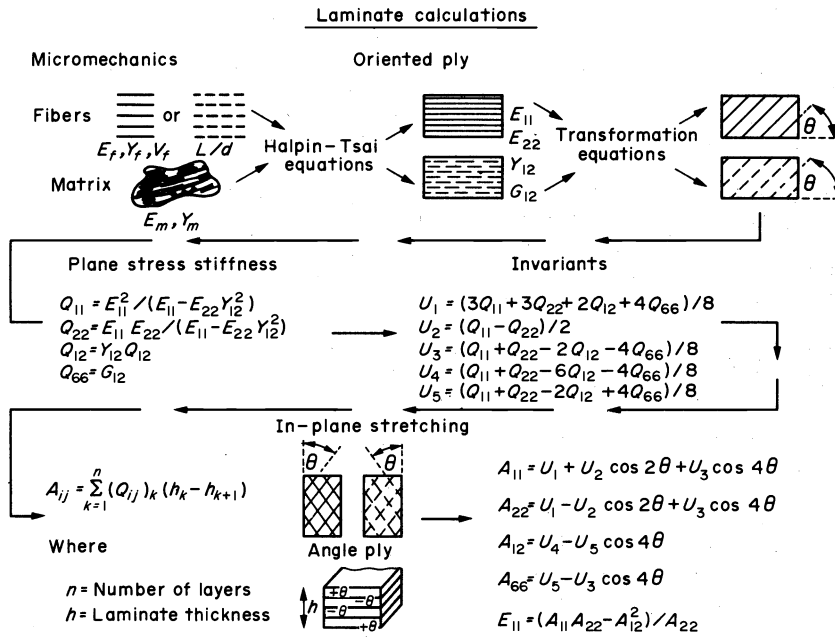


Fig. 13. Example of laminate calculations;  $E_{11}, E_{22}$ , longitudinal and transversal tensile moduli;  $G_{12}$  shear modulus;  $\nu_{12}$  (nu) Poisson's ratio.<sup>6</sup>

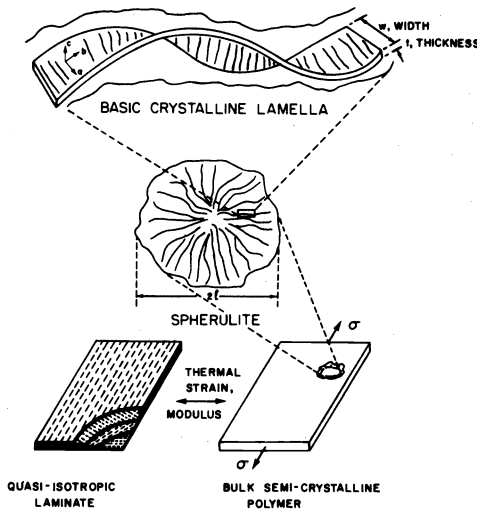


Fig. 14. Composite model for crystalline polymers.<sup>22</sup>

undertaken on how to handle, or how to adapt, continuum mechanics for the case of discrete media, how to calculate crack development and propagation in viscoelastic continua, how to interpret electron microscopy, how to apply X-ray and neutron scattering and electron spin analysis, and how to reconcile molecular theories of work hardening and rupture with experimental results. In the following, I must restrict myself to refer briefly and almost at random to a few cases with which I happen to be acquainted. A concerted critical review of the status of molecular engineering would be a major undertaking, but one which would pay rich dividends.<sup>1</sup>

In the theoretical area, A. Boyd at the University of Utah, working mostly with computer models of the conformations of chain molecules, is now able to calculate the energy of a misfitting polymethylene chain inside a perfect crystal, see Fig. 16, as well as the corresponding energy changes in the latter.<sup>26</sup> Broutman<sup>27</sup> has employed finite element analysis,

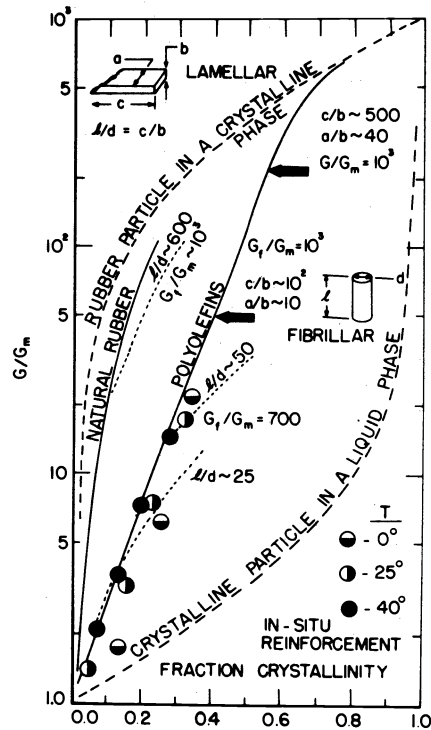


Fig. 15. Experimental relationships between normalized shear stiffness and volume fraction of the crystalline reinforcing phase for natural rubber, crystalline polymers, and model *in-situ*-grown composites of crystallized acetanilide in rubber (circles). The different circles represent different crystallization temperatures (different morphologies).<sup>5</sup>

see Fig. 17, to heterophase systems and has been able to calculate the stress-strain pattern around spherical inclusions in a generalization of earlier methods by Goodier<sup>28</sup> and Oberth<sup>29</sup> for single, or pairs of, spheres. Figures 18 and 19 show the results for the angular stress distribution, and the course of modulus and Poisson ratio

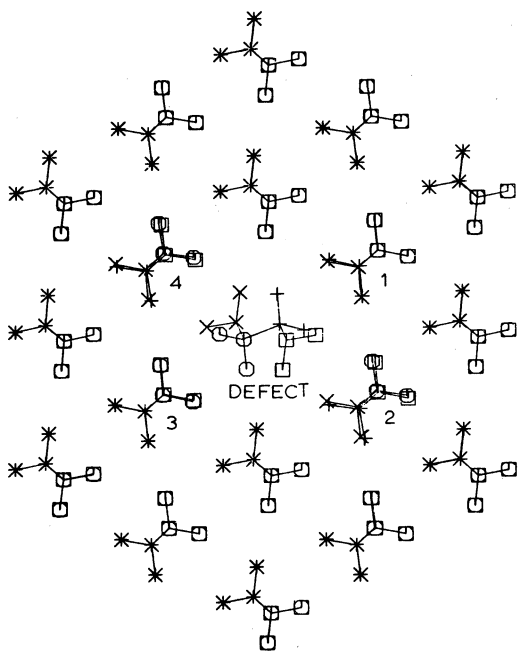


Fig. 16. Site strain model associated with one kink in a chain of a  $C_{20}$  paraffine crystal;  $a-b$  plane.<sup>26</sup>

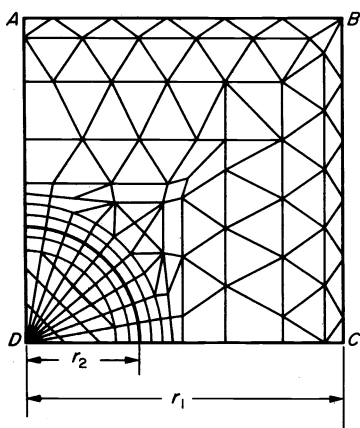


Fig. 17. Finite element grid for  $r_1/r_2 = 0.36$ ; appropriate for volume filling of 3.03% by equal spheres of radius  $r_2$ ; distance between 2 sphere centers is  $2r_1$ .<sup>27</sup>

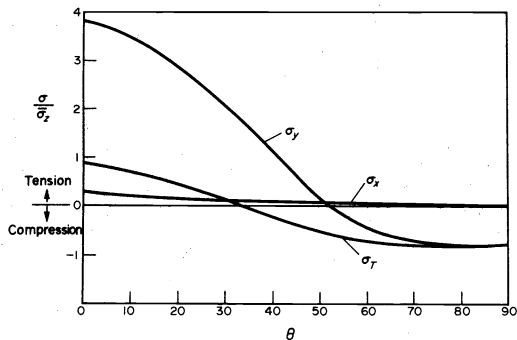


Fig. 18. Interfacial stresses ( $\sigma_i$ ) in a rubber filled polymer ( $v_{fill} = 43.8\%$ );  $\sigma_{x,y}$  stresses normal and tangential, respectively, to spherical inclusion surface;  $\sigma_T$  maximum shear stress;  $\bar{\sigma}_z$  average stress.<sup>27</sup>

Assumed matrix properties  $E=400,00$  psi  
 $\nu = 0.35$

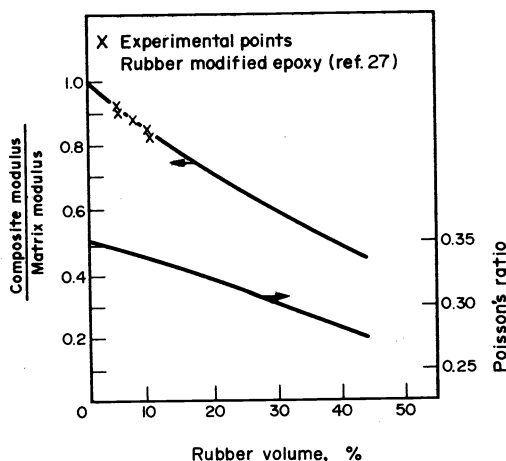


Fig. 19. Modulus and Poisson's ratio for rubber-modified polymer.<sup>27</sup>

with increasing filler volume. Argon<sup>30</sup> developed a molecular theory of kink propagation, Fig. 20, which enables him to calculate not only the energy to move a given dislocation, but also the onset of plastic deformation in glasses and the corresponding yield criteria, in agreement with experimental criteria developed by Sternstein.<sup>19</sup> Yet we have still a long way to go till developments along these lines will lead to a detailed understanding of the molecular motions at the limits of viscoelastic performance and during resistance to crack propagation.

There is consequently, a great need for more morphological studies, during and after deformation, on chain alignment and its time, temperature and pressure dependence as apparent from the nature of failure envelopes.<sup>21,31,32</sup> It looks at this time as if the ultimate properties would follow the Time Temperature Superposition principle. In fact, we see that stress-strain curves proceed on a continuous course right up to rupture. This seems at first difficult to understand, because the TTS is based on bulk properties, whereas rupture phenomena are typically local

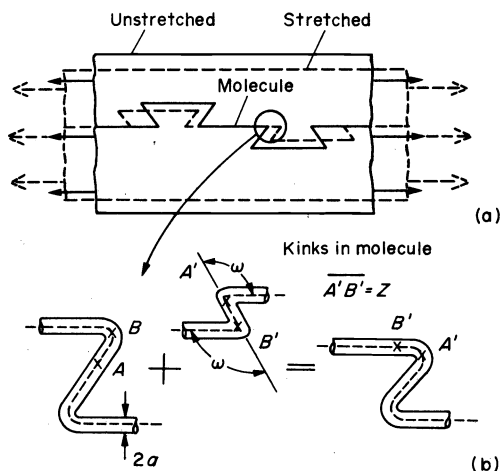


Fig. 20. Kinematic mechanism of local strain production by nucleation of a molecular kink at a pre-existing molecular corner.<sup>30</sup>



events within, or between, small domains. An explanation lies likely again in the observation, born out by electron microscopy,<sup>35</sup> that the material right in front of an advancing crack undergoes the same kind of ultimate deformation as the whole material, if it were to survive up to the same strain in bulk, but this raises the question how TTS remains valid for a changing mobility spectrum.

The most outstanding development of the past decade, from the technological point of view, has been the toughening of rigid plastics by admixing rubber particles. The technique which is by now well understood<sup>20,34</sup> consists of dispersing a lightly crosslinked rubber in monomer, simultaneously polymerizing the latter and grafting it on to the rubber. Electron microscopy has shown that polymerization occurs also inside the original rubber particles which thereby change into cellular clusters of matrix grains enveloped by the elastomer. On stress application, crazes develop in the graft-matrix interphase which travel only as far as to the next rubber-graft particle, into which they enter, branch out and stop. Since the rubber graft particles thus act as strain releasers and also as craze or crack stoppers, the interparticle distances and the ratios of rubber to graft to matrix are critical. The optimum conditions vary from material to material, but by and large particle sizes of the order of 1–5  $\mu\text{m}$  and interparticle distances of the same magnitude are desirable. These values are considerably below those of about 10–100  $\mu\text{m}$ , or more, of accidental nicks or cuts which are known to become dangerous in elastomers. At this time, the nature of the rubber, the method of dispersing it, the choice of the catalysts to produce optimal grafting, and yet more variables are important so that the area is more in the state of an art rather than of a science and a great deal more of exploration is necessary to optimize the production methods of this important class of polymers which combines high moduli, and acceptable reversible strains with ductility, work hardening, and impact resistance.

The lessons from toughened polymers have improved our understanding of the mechanics of the inverse case, namely of strengthening and hardening of elastomeric materials with fillers, i.e. by dispersing particles of high modulus throughout them. In particular, we understand now that the inter-filler particle distances must be shorter than the critical crack length for a given elastomer. We have learned also that filler/elastomer adhesion is necessary to the extent that it must not facilitate void formation at the interface, but allows cavitation to occur at the geometrical maximum stress location, a fractional diameter away from the surface, along the connecting line of two particles.<sup>29</sup> Stress analysis shows that in the matrix of densely filled elastomers there exists not only strain and strain rate magnification,<sup>21</sup> but that also triaxial stresses develop so that failure occurs by, though often nucleated, cavitation.<sup>35</sup> Thus, one of the reasons for the increased moduli in the presence of filler particles is that they cause the material to respond in terms of their bulk moduli rather than their shear or tensile moduli. Further of importance in filled systems is the structure and density and overlap of the interphases, since the restricted mobility of adhering chains itself raises moduli, internal friction and dissipation in rubbers. Notwithstanding the work already mentioned, and older important contributions by Kerner<sup>36</sup> and Hashin<sup>37</sup> to the mechanics of filled systems, more progress in our understanding of the influence of internal friction and slip, i.e. by the irreversible changes in molecular organisation, is required

for engineering purposes, and should come from the study of mechanical loss spectra at large amplitudes. Yet another factor to be studied following the work on moduli, is the contribution to filled elastomeric strength by anisotropic particles, originally isotropically distributed, when oriented in a stress field.<sup>38</sup>

The segmented, or block copolymers offer, of course, new opportunities to regulate interparticle distances, the volume ratios of hard, soft, and interphase composite moduli, and the particle dimensions and geometry, by chemical and thermodynamical means. An important aspect of this methodology is the blending of two polymers with their block polymer, using the latter as a dispersant of one homopolymer in the other. In this way volume ratios can be varied irrespective of sectional molecular weights, i.e. one obtains very stable systems over wide volume ratios. Recent work by Kawai and co-workers<sup>39</sup> advanced the potential uses of these materials by establishing complete ternary diagrams, see Figs. 21 and 22, for e.g. polystyrene and polyisoprene and their blocks. His findings, when further elaborated, will allow rather exact preparations of such polyblends of predetermined moduli, ductility and permissible stresses and strains.

Most industrial applications require mechanical tolerance to multiaxial stress fields. The ability of workhardening in tensile stress fields remains, of course, important since the tensile mode is usually preponderant in front of advancing cracks. However, indigenous uniaxial internal organisation is a disadvantage in multiaxial fields because of the weakness of fibrillar structures in the transverse directions. Thus biaxial orientation is required for biaxial loads, and an isotropic, but potentially fibrous one for triaxial fields. So far, process engineers have achieved great success in producing biaxial films and sheets. Figure

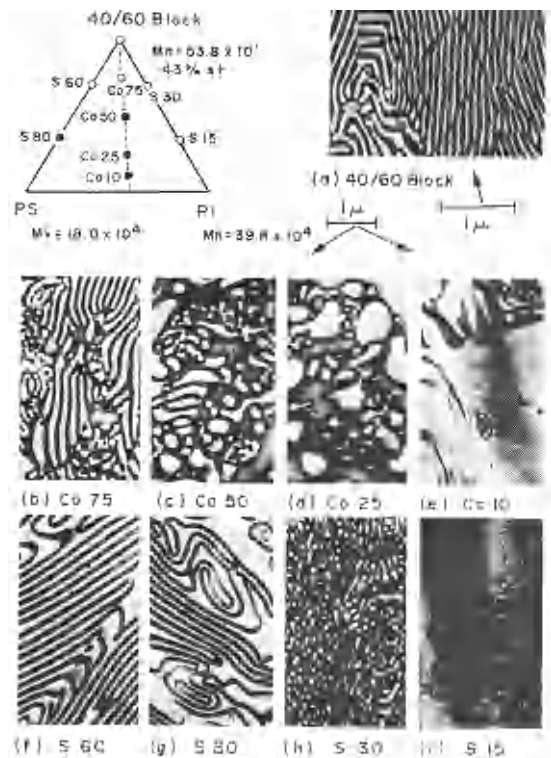


Fig. 21. Triangular polystyrene-polyisoprene diagram representing the composition in weight fractions of ternary or binary mixtures and electron micrographs of ultrathin sections of films cast from 5% toluene solutions and stained by  $\text{OsO}_4$ .<sup>39</sup>



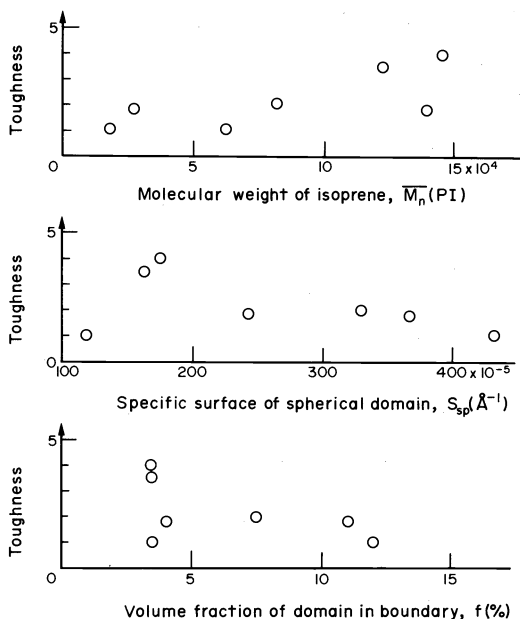


Fig. 22. Toughness (area under stress-strain curve) of blends of polystyrene-polyisoprene-PS/PI Block 40/60 as function of: mol. weight of isoprene segment; specific surface of spherical domain, and of volume fraction of domain boundary phase.<sup>39</sup>

23 reproduces a plot of impact strength of polybutene films as a function of degree of biaxial orientation, and Fig. 24 shows diagrammatically the factors involved in manufacturing such films by a simultaneous blowing and stretching method.<sup>40</sup> Important are: the ratios of extruding speeds from the annular die to the draw speeds of the nip rolls, the blowing pressure, the melt temperature, and the air temperature. They regulate the optimal draw ratio and degrees of orientation near the frost line where the consolidation of the radially and tangentially expanding film occurs.

Even more intricate and advanced engineering methods have recently been developed for blowing bottles. At first, a cylinder is molded which subsequently is reheated to just below the glass transition temperature. The cylinder is extended at differential rates so that its wall thickness is programmed along its length, and is expanded by blowing it against the bottle mold. The resulting bottle varies not only in wall thickness at lip, neck, main body, and bottom, but also in molecular orientation which is preponderantly biaxial along the hoop stress lines in the middle and more radial at the two ends of the bottle. By such specific

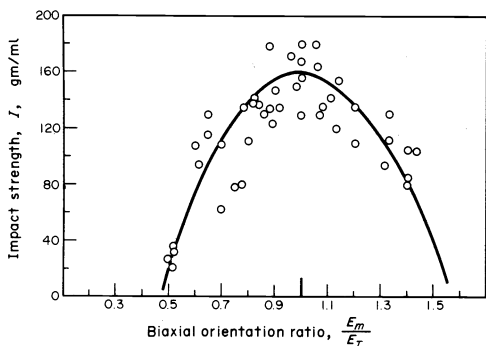


Fig. 23. Impact strength vs orientation balance;  $E_m$  direction of mold extrusion;  $E_T$  transverse direction.<sup>40</sup>

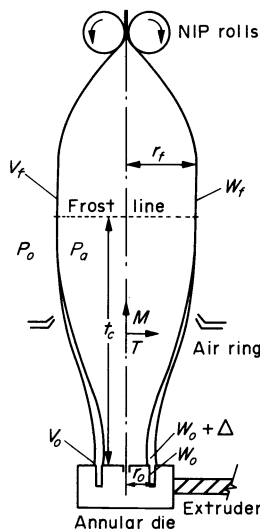


Fig. 24. Sketch of tubular blown film line.<sup>40</sup>

engineering, e.g. a basically rather brittle copolymer of styrene and acrylonitrile could be used for the production of quite acceptable soft drink bottles.

Other ways for producing desired orientations include extrusion of polymeric melts, or of concentrated solutions, which are already preoriented. One way, of course, is to subject the extrudate to a suitable flow field, but another method recently pioneered by Du Pont is to employ spontaneously anisotropic melts, as in the case of some of their high melting polyimides. In a related process, Fig. 25 shows the preorientation in extruded pitch which eventually becomes carbonized and thereby produces graphite fibers of very high internal coaxial orientation.<sup>41</sup>

The greatest difficulties, naturally, are encountered in designing materials of a triaxial strength beyond their matrix cavitation stresses which are always seriously lowered by flaws and impurities. Polyblends, block copolymers, and filled plastics are, of course, early forms of such materials, especially, if a high modulus, asymmetric, phase is used and is isotropically oriented. If, though, a truly fibrous filler were used, the principal difficulty would be that, say, cylindrical elements would have to have aspect ratios of 100 or more before the stress concentrating effects of the fiber ends are overcome by the reinforcing effects of the fibers themselves. It appears, then, that one we will have to learn to use long, rather than staple, fibers, building isotropic composites as e.g. represented by a three dimensionally matted or woven fiber pack impregnated by a tough resin. An alternative approach to the same problem has been pioneered by Alfrey<sup>42</sup> who has been able to co-extrude and colaminate up to hundreds of films, only 10- $\mu\text{m}$  thick or less, at a time. By stacking such co-laminates in cross ply fashion and by cementing them with interlayers of an adhesive capable of fibrous extension perpendicular to the bound layers, again a 3-dimensional, reinforced or self-reinforcing, system could be designed. Yet another technique for 3-dimensional strength is based on an observation some time ago<sup>43</sup> that, extruding from a wider container through a narrow orifice, very interesting and multiple back flow patterns develop as shown in Fig. 26. Suitable engineering is capable of exploiting this tendency by the application of baffles and channels, achieving a similar backfolding as in

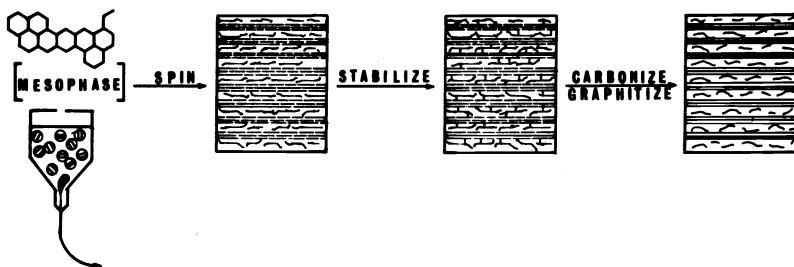


Fig. 25. Mesophase pitch process for carbon fibers. A pitch which is partially isotropic and partly liquid crystal is melt-spun to give a preferred orientation to the liquid crystal elongated domains. The fiber is oxidized to thermoset the isotropic pitch, and the fiber is heated to carbonize and develop the structure.<sup>41</sup>

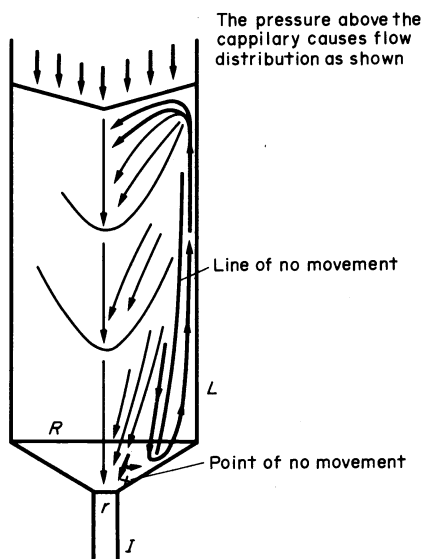


Fig. 26. Sketch of observed flow in barrel above extrusion die, showing split of flow near exit and recirculation near wall.<sup>43</sup>

the layering of a multiple leaf dough, or a Damascus sword. Such layered structures could again be reinforced by long fibers and subsequently be pressed into desired forms whereby the molecular orientations in matrix or of the reinforcer could be arranged so as to support best the anticipated load pattern. Altogether, the method of coextrusion of jets, films, or tubes is so far little developed but promises to open many new design possibilities.

Last, I want to mention two methods which are as yet little explored for polymeric systems. One comprises various techniques to prestress or, conversely, to anneal formed polymer pieces by surfaces quenching or heating and producing a state of internal, or superficial, prestressing, Fig. 27.<sup>44</sup> The heat developed by friction during fast extrusion, or the heat of crystallization arising during cold drawing and orientation hardening<sup>45</sup> could also be used for tempering purposes. According to the other method, the finished parts, or specimen, are subjected to proof testing, a practice well developed for metals and only recently explored for polymers.<sup>46</sup> A member or part whose performance one wants to be fail-safe during a specified time and conditions is subjected to more strenuous conditions for a specified test period and then inspected for damage. Provided none is found which would be likely to influence the life expectancy, the specimen may be anticipated to work safely under less strenuous conditions, Fig. 28. It should be mentioned that the concept of

damage and of damage influence on polymeric behaviour is still in its infancy. The so-called constitutive equations in their more sophisticated form take material history and memory into account, but do not include structural changes in the material such as crystallization, plastic flow, molecular rupture, cracks, or other changes in specimen integrity. Theoretical and experimental work is in progress to formalize the concept of damage within the frame of constitutive equations,<sup>47</sup> and also to follow the progress of such damage, as can be measured by electron spin resonance, produced by broken chain ends as a function of strain, rate and time;<sup>48</sup> see e.g. Fig. 29.

In conclusion, I hope to have elaborated in a sufficiently

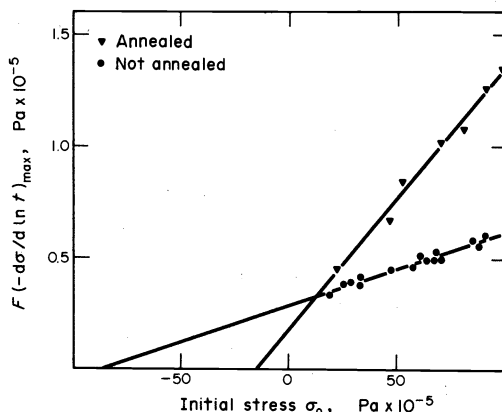


Fig. 27. Determination of internal stress in injection molded ABS resin, as molded and after annealing at 80°C for 5 days; plot of minimum slope of stress decay curve (stress vs ln time) against initial stress.<sup>44</sup>

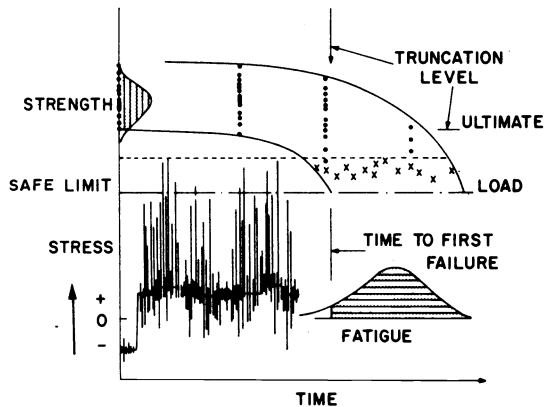


Fig. 28. Illustration of relationship between static fracture strength, load history, fatigue, and fail-safe time.<sup>46</sup>

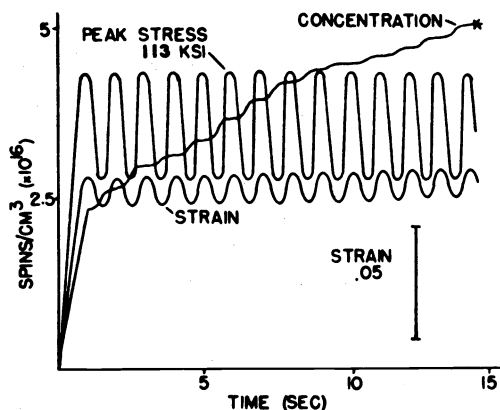


Fig. 29. Stress, strain and electron spin signal concentration vs time for cyclic loading superimposed on a static load.<sup>48</sup>

comprehensive way on the emerging awareness of the importance of molecular organisation, its accidental forms, and on the ways by which we could shape, influence, and characterize it to conceive and derive new design methods for new uses of macromolecular materials. If again we may take nature as our guide, we should look at the structure, architecture and chemistry of wood, bone, hair, or of membranes as outstanding examples of molecular organisations for structural and, of course, metabolic and biological purposes. Molecular engineering for the production of molecular composites to suit predetermined objectives, therefore, beckons as one of the outstanding and intriguing goals in chemistry, physics, mechanics, and molecular biology.

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