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FRACTURE IN HIGH POLYMERS: A MOLECULAR INTERPRETATION

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ABSTRACT

The formation of free radicals during flow and fracture of high polymers - now widely documented - has called attention to the load bearing capacity of individual chain segments. In this paper the effect of the density of primary bonds and of chain lengths, orientation, and interaction on sample strength is discussed. The extent is studied to which axial stresses can be transferred onto chains through the retractive forces of a crystal potential or through frictional forces. The results are related to the concentration of chain breakages as obtained from ESR-investigations. The contributions of chain scission and slip to the energy dissipated in subcritical growth of a planar crack are analyzed in terms of polymer morphology for glassy polymethyl methacrylate (PMMA) and semicrystalline polyethylene (PE), polypropylene (PP), and polyamide (PA). The studies show that the backbone chains have a limited capability to pick up axial stresses in shear (with stress transfer lengths of between 10 nm and more than 100 nm). An accumulation of critical axial loads is possible, therefore, only at chain segments of extended conformation and within matrix volume elements of a size larger than the stress transfer lengths. The nearly "complete" orientation of molecular chains (as in extended chain PE or in Kevlar ®) increases the homogeneity of the shares of axial load carried by the chains. By virtue of this high homogeneity, however, do strength and fracture toughness depend strongly on the intermolecular attraction.

INTRODUCTION

Polymeric materials are composed of highly anisotropic, generally quite flexible, statistically coiled molecular chains. In the chain axis direction atoms are bound by primary valencies which provide fully extended chain segments with extraordinary strength ($\sigma_f > 5$ GN/m^2) and stiffness ($E > 50$ GN/m^2). In the lateral direction chains interact with each other through secondary (van der Waal's) bonds which are roughly two orders of magnitude "weaker". The local forces involved in material separation within a polymeric body should depend, therefore, on the strength and the degree of utilization of the primary bonds. In this paper the effect of the existence and the decay of primary bonds on sample strength is investigated along three different routes:

- parametric correlation between bond density and macroscopic strength or stiffness

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- bond loading mechanisms
- consideration of energy and kinetics of defect development

BOND DENSITY AND MACROSCOPIC STRENGTH

Many authors feel that the existence and volume concentration of the strong primary bonds already determine the rigidity and strength of solids including polymers. Holliday et al [1] have looked under this aspect on the relative volume density N_r of main network bonds; N_r is given by polymer density times number of network atoms in the repeat unit divided by molecular weight of a repeat unit. The term N_r varies between less than 0.01 for bulky polymeric chains and 0.58 for diamond. The bulk moduli, Young's moduli, hardness values and cubical coefficients of thermal expansion of the more than 50 organic and inorganic polymers investigated at room temperature exhibit a strong correlation with N_r. In Figure 1 the best fit curves drawn by Holliday for Young's modulus and Brinell hardness values-BHN are shown (the actual N_r values - except for those of the graphite-like structures - fall into a narrow band along the curves having a width of ± 0.05). The nearly identical shapes of the upper portions of both curves suggest that hardness (compressive yield strength) and elastic modulus depend in the same way on the concentration of primary bonds. In fact for the points on the curve with $N_r > 0.08$ (mostly organic thermosetting resins or inorganic polymers) the ratio of BHN value and E has a constant value of 0.0625.

For values of $N_r < 0.08$ (thermoplastic materials) the correlation between mechanical properties and bond density is much less pronounced although the steep slopes of the shown curves tend to make the scatter of the actual data points less apparent. The main reason for the lack of good correlation certainly is the fact that thermoplastics are not a covalently interconnected network. The molecular stiffness and strength can be utilized only to that extent which intermolecular attraction and segment orientation do permit (cf. Table 1 for the differences in elastic moduli of chains, highly oriented fibers, and isotropic solids).

Another parametric approach to characterize the effect of the density of main chain bonds on the mechanical properties was proposed by Vincent [2]. He pointed out that the experimental test conditions had to be chosen in such a way that comparable mechanical excitation of said bonds does indeed take place. He suggested that the brittle point temperatures would be suitable, that is the temperature where brittle failure changes to a ductile failure. As indicated in Figure 2 he has related the number of backbone bonds per unit area (i.e. sample density times length of repeat unit over weight of repeat unit) to the critical tensile strength of (isotropic) polymers. A linear relationship exists between critical sample strength and bond packing density which does not seem to depend on the chemical nature of the bond. From the slope of the straight line the critical strength (in MN/m^2) of the isotropic polymers is obtained as 26.8 times the number of backbone bonds per nm^2. In highly oriented textile fibers this figure is much larger and amounts to between 100 and 250, in aromatic polyamide fibers (Kevlar-49) it reaches about 650. This should be compared with the theoretical value for fully oriented chains of infinite length which is about 3000, since the axial load to break a molecular chain of any one of the species listed in Figure 2 is of the order of 3 nN.

In other words in isotropic thermoplastics at the point of brittle failure only a minute fraction - of less than 1% - of all main chain bonds is fully strained. Under these conditions onset of unstable crack propagation is determined by the magnitude of intermolecular attraction. Reinterpreting Vincent's data we must say that it is not the number of backbone bonds per unit area and their accumulated strength which determines macroscopic strength but the level of intermolecular forces; the latter benefit from a closer packing.

The effect of finite chain length (molecular weight) and degree of chain orientation on fiber strength has been widely investigated, the general observations can be briefly summarized and illustrated by Figure 3 for polyamide 6 (PA 6) fibers.

In a low molecular weight material chain slip occurs readily so that the sample strength depends solely on the strength of intermolecular attraction. Noticeable macroscopic strength is only obtained if the molecular weight is sufficient to permit physical cross-links through entanglements or chain folds between several chains. In the range of molecular weights between 1.5 and 3.10^4 g/mole fiber strength increases with molecular weight, whereas at still higher molecular weights the effect of the increasing number of defects introduced in processing such a fiber tends to outweigh the effect of the decreasing number of chain ends (Figure 3, curve I). It is also indicated in Figure 3 (curves I - IV) that high strength values of the high molecular weight materials are only obtained if high degrees of orientation had been achieved through drawing at elevated temperatures T_d (3). The effects of crystal structure and molecular weight on macroscopic tensile strength are shown by curves V and VI (4). In the strongest of these PA 6 fibers the average main chain bond is stressed to more than 5% of its theoretical strength. It is primarily the behavior of these materials that will yield information on the role of individual molecules in fracture initiation and propagation.

Highly oriented semicrystalline fibers have a microfibrillar substructure as indicated in Figure 4. The microfibrils contain folded chain crystallites as most important structural elements. In addition they contain amorphous regions with coiled chains and chain ends (ciliae). Loading such a microfibrillar structure in the direction of orientation results in the shear loading of the microfibrils, the dilatational loading of the amorphous regions, and the stretching of molecules connecting adjacent crystallites, the so-called tie molecules. It has been shown in detail by electron spin resonance (ESR) investigations (6,7) that these tie molecules are loaded beyond their strength limit and rupture well before the onset of unstable macroscopic fracture.

In the following we will discuss the possible effect that the loading and rupture of a chain segment has on the fracture resistance and on the energy to form the fracture surface. In order to do so we have to study the forces and displacements necessary to load a chain and the energy dissipated by the freed chain ends and by the matrix surrounding them.

AXIAL LOADING OF CHAIN SEGMENTS

The flexibility of stressed polymeric chains has two consequences: large axial stresses are only built up on almost straight segments, and bending stresses are not transmitted over a distance of more than a few nm. The transmission of large axial stresses onto straight chain segments through static shearing forces was recently treated by Kausch and Langbein [8] who assumed that the elastic displacement u of a chain section (length L, modulus of elasticity E) against the cohesive energy in a crystal lattice has a potential $V(u) = W(1 - \cos(2\pi u/d))/L$ where d is the length of the unit cell and W a potential energy constant. The largest stress that can be transferred to a chain by a regular periodic potential is

$$\psi_{max} = 2\sqrt{WE/qL} \tag{1}$$

where q is the chain cross-section. For polyethylene (PE) one obtains 9.4 GN/m^2 ($E = 290$ GN/m^2, $q = 18.2 \cdot 10^{-20}$ m^2, $W/L = 1.382 \cdot 10^{-11}$ N).

In the more general case of a kinked chain extending in one direction (z), and being composed of different sections i, with almost identical $E_i \cdot q_i$, but arbitrary matrix interactions W_i/L_i, we have for small stresses

$$\psi = E_o \frac{du}{dz} = u_o \frac{\gamma}{L} E_o \tag{2}$$

where u_o and E_o refer to the section experiencing the largest elastic displacement, L is now the end-to-end distance, and γ is a parameter given by the expression:

$$\gamma = \pi \sqrt{n \sum_1^n W_i / E_i q_i L_i} \tag{3}$$

It should be pointed out that the attainable level of axial stresses ψ is not so much determined by the average cohesive energy density within the crystallite but by its gradient W_i/L_i. The largest stress occurs for $u_o = d/2$ and comes to $\gamma E_o/\pi$. Large stresses in static tension may, therefore, only be generated if γ and E_o are large. In PE γ has a value of 0.10, i.e. 0.05 per chain atom; in 6 polyamide (PA) γ reaches 2.56; i.e. 0.183 per chain atom. The difference between PA and PE is mostly due to the strong and localized action of hydrogen bonds established between chain and matrix. Using the above values of γ, the largest stresses exerted on completely extended chains, which are partly embedded in two crystal lamellae, separated by an amorphous region (tie-molecules) come to 9.4 GN/m^2 (PE) and 22.9 GN/m^2 (6 PA).

The axial stress of a tie-molecule is essentially constant within the amorphous layers, and decreases within the adjacent crystalline regions due to the above described shearing forces. The elastic displacement of the tie-molecules relative to the crystal lattice reaches a maximum (u_i) at the interface between crystalline and amorphous regions, and decreases within the crystal, according to equation (2), to 0.01 u_i within $\Delta z = 3.1$ nm in PA 6 and within $\Delta z = 11.6$ nm in PE.

In the dynamic loading of a network, or a solution, the axial force f on a chain (of arbitrary conformation and elastic modulus E) is proportional to the "monomeric friction coefficient" ζ_o and to the difference between the respective axial displacement rates $\mathring{u}_m$ and $\mathring{u}_c$ of matrix and chain:

$$f = \zeta_o (\mathring{u}_m - \mathring{u}_c) = - EqL_{mon} \, d^2u_c / dz^2 \tag{4}$$

where the z axis indicates the direction of slip, L_{mon} is the length of a monomer, and L the chain end-to-end distance. In a solid, under stationary conditions, $\mathring{u}_m$ is a constant fraction (p) of $z\mathring{\varepsilon}_m$, and $\mathring{u}_c \to 0$; equation (4) can thus be integrated to give:

$$\psi = Edu_c/dz = \frac{\zeta_o p \mathring{\varepsilon} \rho N_A}{M_{mon}} \left(\frac{L^2}{8} - \frac{z^2}{2} \right) \tag{5}$$

where M_{mon} = monomer molecular weight, ρ = density, and N_A = Avogrado's number. Equation (5) predicts that axial stresses are proportional to the square of the chain length, i.e. to $(M/M_o)^2$ and to strain rate. Chain scission should occur once $M^2\mathring{\varepsilon}$ exceeds a critical value. Monomeric friction coefficients in solids are not easily available and are extremely temperature dependent. At the respective glass transition temperatures (T_g) of polystyrene (PS), polyisobutylene (PiB), polyvinyl chloride (PVC), polyvinyl acetate (PVAc), and polymethylacrylate (PMA) they range from 0.1 to 1700 Ns/m, while at T_g + 100 K they range from 0.3 to $200 \cdot 10^{-10}$ Ns/m [9a]. The friction coefficients at T_g are sufficient to produce chain stresses of 20 GN/m^2 (at strain rates of 0.001 s^{-1}) within extended segments of 11 to 1500 Å length.

With solutions, the ζ_o values are essentially determined [9b] by $[\eta] \, \eta_s / \overline{r_o^2}$, i.e. polymer intrinsic viscosity, solvent viscosity, and mean square end-to-end distance. At shear rates above 600s^{-1} and molecular weights above $1.6 \cdot 10^5$ kg / kmole the friction at shears are sufficient to cause chain scission [10].

We assume that chain scission is thermo-mechanically activated, i.e. a chain segment containing n_c weakest bonds of energy U_o, and carrying at its ends a constant stress ψ_c will, on the average, break after time τ_c given by

$$\psi_c \, (U_o, n_c) = (U_o - RT \, \ell n \omega_o n_c \tau_c) \, / \beta \tag{6}$$

where R, T, ω_o and β are gas constant, absolute temperature, bond vibration frequency, and activation volume for bond scission respectively [11]. A 50 Å nylon segment, for instance, at room temperature, has an instantaneous strength of 20 GN/m^2 (taking U_o = 188 kJ / mole, $\omega_o = 10^{12}$ s^{-1}, $n_c = 10$, $\tau_c = 6$ s, $\beta = 5.53 \cdot 10^{-6}$m^3/mole). If in straining a segment, a stress of 20 GN/m^2 is maintained for a period of 6 s the segment has a probability of failure of 1 - 1/e = 63%.

In order to determine the contribution of breaking chains to fracture surface energies we need to estimate the expected number (area and volume concentration) of chain breakages as a function of intermolecular attraction and chain packing. In the idealized case of fully oriented, non-interacting chains of length L and cross-section q the breakage of each chain affects a volume Lq. The maximum volume concentration of chain breakages is 1/qL, i.e. 1.4 to 5.10^{-20} m^{-3} in L = 1 cm specimens. The concentration in a fracture surface layer of thickness r_p is consequently r_p / qL, and under the specified conditions r_p must correspond to L/2. The area concentration amounts, therefore, to 0.7 to $2.5.10^{18}$ chain breakage per m^2 of fracture surface.

Next we consider the case of chains mutually interacting within a semi-crystalline sandwich structure as shown in Figure 4 and neglect for the moment the microfibrillar substructure. The breakage of one chain segment does relieve axial stresses over the length of the segment within one amorphous region (L_a) and a distance of 2 Δz in the adjacent crystalline regions. The fraction of fully extended and, therefore, breakable chains, within an amorphous region can be estimated from the elastic moduli E_a of the amorphous region, E_{iso} of the isotropic solid, and E_c of the chain. It can be no larger than $(E_a - E_{iso})/E_c$. Applying the data of Table 1 to a PA 6 sandwich structure with a degree of crystallinity of 50% one obtains the fraction of extended segments to be smaller than 0.008. The upper limit for the volume concentration c_v of breakable chains in PA 6 is, therefore, $(E_a - E_{iso}) / E_c q(2\ \Delta z + L_a) = 4.10^{24}\ m^{-3}$. For PE one derives $1.7 \cdot 10^{23}\ m^{-3}$.

The apparent area concentration c_a again depends on the depth (r_p) of heavily strained material which varies between a few µm in milled or ground material (6) and total sample length in uniaxially stressed fibers; with r_p = 2 µm we expect $c_a = r_p c_v$ to be $3.4 \cdot 10^{18}\ m^{-2}$ (PE) and $8 \cdot 10^{18}\ m^{-2}$ (PA) respectively.

The microfibrillar substructure of the semicrystalline fiber [12] leads to a further non-homogeneity in stress distribution since the fibril ends are free from axial stresses. The axial stresses are only gradually transmitted onto the fibrils through interfibrillar shear stresses (τ) over a length $L_\varepsilon = E_f\ \varepsilon\ d/2\tau$. Whereas the fibril diameter d ranges between 10 and 50 nm for a large variety of fibers [12] data on fibril elastic modulus E_f, fibril length, and τ are less certain. In any event the microfibrillar substructure has the effect of reducing the number of load carrying chain segments and introducing fibril slip as a means to alleviate local stress concentration.

We may compare the above values with the volume concentration of chain breakages actually determined by means of ESR technique. From the concentrations of free radicals [6] formed in uniaxially stressed fibers we obtain breakage concentrations from $< 10^{20}\ m^{-3}$ (PMMA, PS), $0.01 - 2.10^{22}\ m^{-3}$ (PE, PET) to about $0.5.10^{24}\ m^{-3}$ (PA 6, natural silk). The latter value is a factor of 8 smaller than the theoretical limit calculated for a regular sandwich structure. The number of breakable chains is decreased, however, by all deviations from regularity. It is decreased notably by the variation of the lengths of the extended chain segments and by intracrystalline and interfibrillar slip [6]. In view of this fact we may say that the chain breakage concentrations observed in PA 6 are the maximum to be expected for such a microfibrillar sandwich structure.

The observed surface concentrations of chain breakages in ground or milled polymers are of the order of $1 - 20.10^{16}\ m^{-2}$, roughly two orders of magnitude below the upper limit [6].

CHAIN ENERGY CONTRIBUTIONS TO CRACK RESISTANCE

In the context of the present investigation on the particular role of the chain backbone in material loading and disintegration we consider a slowly advancing planar crack (mode I). In the material ahead of the crack tip a sequence of energy consuming processes take place (cf. Figure 5):

- homogeneous energy elastic straining of the matrix and partial relaxation of the ensuing stresses (region A)
- initiation of non-homogeneous deformation, i.e. plastic deformation, void formation, chain scission or craze initiation (line or surface B)

- heterogeneous deformation until material disintegration through chain separation and/or scission is completed (region C)
- retraction of strained chain segments, coils, fibrils, and matrix material adjacent to the now well defined crack (region D)

The density of stored elastic energy, $w = \sigma_y^2/2E$ in the homogeneously strained region (A) increases with decreasing distance r from the crack tip as $1/r$; the energy density is limited by the onset of non-elastic deformation. In PMMA the maximum strain energy density will be of the order of 0.1 to 0.5 MJ/m^3 which is an insignificant fraction of the cohesive energy density of 500 MJ/m^3. It is worthwhile to point out that at these stress levels the stored elastic energy is absolutely insufficient to achieve chain segment separation directly and prior to chain reorientation.

If a crack were to grow solely by the separation of two layers of chains to a distance beyond their mutual attraction, say, 0.2 nm and solely at the expense of the stored elastic energy it would require the cooperative transfer of the energy stored within a 200 nm layer to the boundary of that layer. Such a process is absolutely unlikely to occur, irrespective of chain length, strength, or conformation.

The purely elastic separation of an individual chain segment becomes more likely if the thermal energy fluctuation is taken into consideration; at room temperature the thermal energy of a PMMA monomer unit reaches 25 kJ / mole, the energy to create new surface by separation of two monomer units is $2\ \gamma \ell_m \sqrt{q}$, here 8 kJ / mole (surface tension γ, monomer length ℓ_m, chain cross-section q). There is, therefore, a finite probability for the thermal activation of a void which will grow by further activation to the extent repulsive forces and chain entanglements do permit.

With stress level in region A being as it is it can be stated that the loss of stored energy through stress relaxation during crack propagation does by no means account for the observed energy dissipation in fracture formation. Without giving detailed proof for all environmental conditions, we may say that in all generality major energy dissipation begins with the onset of non-homogeneous deformation (B).

In non-oriented glassy polymers this onset is more determined by intermolecular attraction and chain mobility than by chain length, strength, or conformation; the latter properties come to bear, however, in region D through the amount of load carried by the reorganizing "network" of chains and through the extent to which the network can be deformed before material separation occurs. A molecular representation of the initiation of non-homogeneous deformation, i.e. of void (B_1) and microfibril (B_2) formation is given in Figure 6.

Under these circumstances the main effect of a long chain backbone in an unoriented polymer cannot be seen as to raise the local stress at which plastic deformation initiates but in minimizing - or even temporarily cancelling - the effect of material inhomogeneities or cracks as stress concentrators. Chain length and chain strength are not effectively utilized in non-oriented systems.

In partially oriented microfibrillar systems as in the previously discussed semicrystalline fibers the situation is different. The microfibrils as we have seen utilize chain strengths to about the level given by segment orientation and attraction. A large number of chain segments is completely extended. Under load these segments will be elastically stretched in axial direction. The less folds, kinks, chain ends, and other irregularities there are, the higher the sample's Young's modulus E. The effect of the extended chain segments on the energy of fracture surface formation is threefold. With breakage of a chain the elastic energy is dissipated which was stored in the chain itself (chain relaxation). The matrix relaxes which has exerted the critical axial stresses onto the chain (loss of strain energy) and energy is expended to break the chemical bond.

The loss of matrix strain energy in PA 6 and PE must be smaller than 40 MJ/m^3, the total elastic energy at 10% elastic strain. The elastic energy stored in the chain itself can be derived from equation (5) at chain stress ψ_c as:

$$W = \int_{-L/2}^{+L/2} \psi_c^2 \, qdz/2E = 4\psi_c^2 \, qL/15E \qquad (7)$$

This means that W/qL, the strain energy density in the volume occupied by the stressed chain, amounts to 530 MJ/m^3 in a completely extended 6 PA chain (in comparison: the cohesive energy density if 750 MJ/m^3 and the strain energy dissipated up to the point of chain scission in the bulk of the surrounding matrix typically 50 - 200 MJ/m^3). Chain scission events are, therefore, justly termed "micro-explosions" by Zhurkov and his co-workers. On the other hand at a concentration of $0.5 \cdot 10^{24}$ m^{-3} the total chemical energy of the broken bonds amounts to only 0.15 MJ/m^3, the relaxation of the freed chain ends to 0.32 MJ/m^3. In a fracture surface layer of 2 μm depth a fraction of 0.3 J/m^2 of dissipated energy would consequently be accounted for by broken main chain bonds, a fraction of 0.64 J/m^2 by chain end relaxation. Both terms are only slightly larger than the surface tension γ (0.04 J/m^2) and small compared to the crack resistance, even in the subcritical region of crack propagation (cf. also Table 1).

These semicrystalline fibers, therefore, derive their strength from a notable stiffness (due to highly oriented chain segments) and from the fact that chain segments as well as micro fibrils must be loaded in shear over appreciable lengths and to high stresses. In this process strain hardening and energy dissipation through slip occur rendering these materials a high stability against stress concentration on a molecular level.

Again a different situation exists with ultra-high modulus fibers. For instance in Kevlar ® 49 with E = 144 GN/m^2 or extended chain polyethylene with E from 50 to 100 GN/m^2 [14] the chains are almost completely oriented. No strain hardening and hardly any favorable redistribution of load through slip are to be envisaged. In the absence of interfibrillar slip can the failure of a chain only have the consequence that the strain energy of the lattice and the axial stresses of the surrounding chains are increased. The chains at the apex of a crack rapidly accumulate large axial strain energy which they partly transfer upon neighbouring chains and on the chain interaction potential. In the case of moderate interaction potential (PE) a large number of chains at the apex is highly loaded and not capable to carry appreciable excess loads. Scission of a sequence of neighbouring chains may initiate the successive failure of the others - the material is highly brittle (fracture at 0.5 to 1% strain). In the case of strong interaction potential (PA) the capacity for storage of extra energy in the hitherto only partially loaded neighbouring chains stabilizes many of the initial chain scission events. Work on this subject, particularly including also interfibrillar slip as a failure mechanism, is in progress.

CONCLUSION

As a result we state that in short-time loading of semicrystalline fibers and bulk amorphous polymers chain molecules do not significantly contribute to the fracture surface energy through the energies of bond breakage and elastic retraction. Large values of chain length and chain strength contribute, however, to reduce the effect of material inhomogeneities as stress concentrators through the plastic deformation necessary before material separation occurs. In ultra-high modulus fibers chain back-bone properties are directly utilized to an extent strongly determined by intermolecular interaction.

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Table 1 Mechanical Properties of Chain Molecules and Polymeric Solids*

Polymer, Abbreviation	Chain Molecule			Oriented Fiber		Isotropic Solid		
	Monomer mol. weight M_o (g/mole)	Monomer length L (nm)	Young's modulus E_c (GN/m^2)	Young's modulus E (GN/m^2)	Strength σ_b (MN/m^2)	Young's modulus E (GN/m^2)	Strength σ_b (MN/m^2)	Critical stress (2) σ_c (MN/m^2)
1. Polyethylene PE	28	2.53	290					
high density				8	(200)	1	27	160
low density						0.2	13	
extended chain PE (14)				50-100	480			
2. Polypropylene PP	42	6.5/3	41	6-9		1.2-2.4	33	98
3. Polyethylene terephthalate PET	192	10.8	74-137	20-25	800-1400	3	53	155
4. Polyamide PA								
Polycaprolactam PA 6	226	17.2	200	5-8.5	400-1000	1.2	61	(179)
aromatic (Kevlar)	119	6.6	180	144	3000			
5. Polymethylmethacrylate PMMA	100	2.11				3-4	70	68

*Reference values of technical polymers at room temperature (critical stresses refer to temperature of ductile-brittle transition); data from D.W. van Krevelen, Properties of Polymers, Elsevier Publishing Company, Amsterdam, 1972.

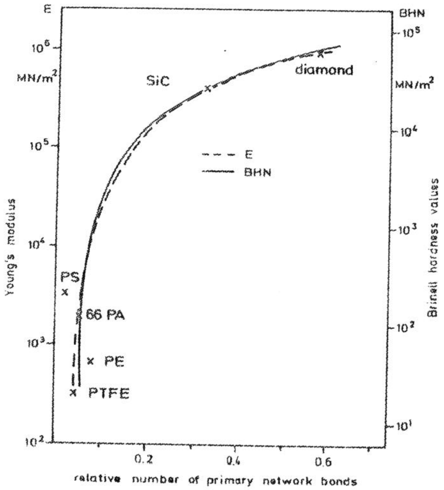


Figure 1 Young's modulus E and Brinell Hardness values BHN of organic and inorganic materials (after Holliday et al)

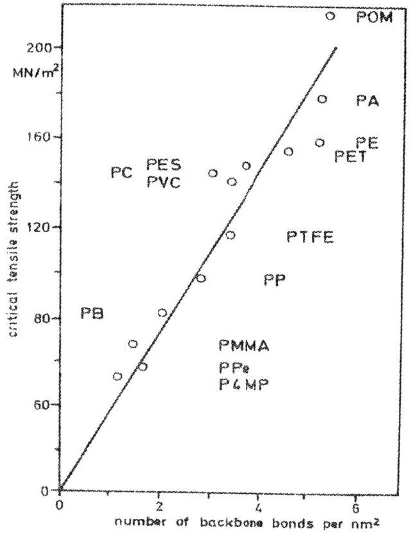


Figure 2 Critical tensile strengths of isotropic thermoplastic polymers as a function of chain packing density, i.e. sample density times length of repeat unit over weight of repeat unit (after Vincent)

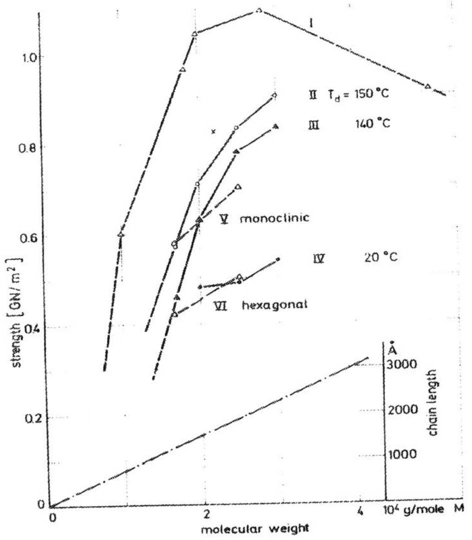


Figure 3 Effect of molecular weight, drawing temperature (T_d), and crystal structure on strength of 6 - polyamide

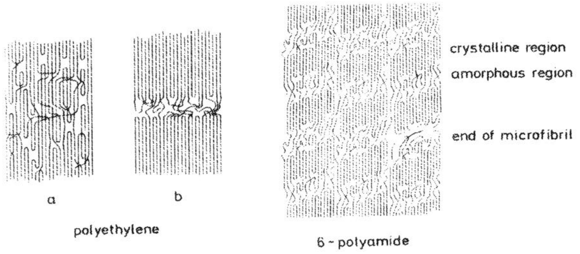
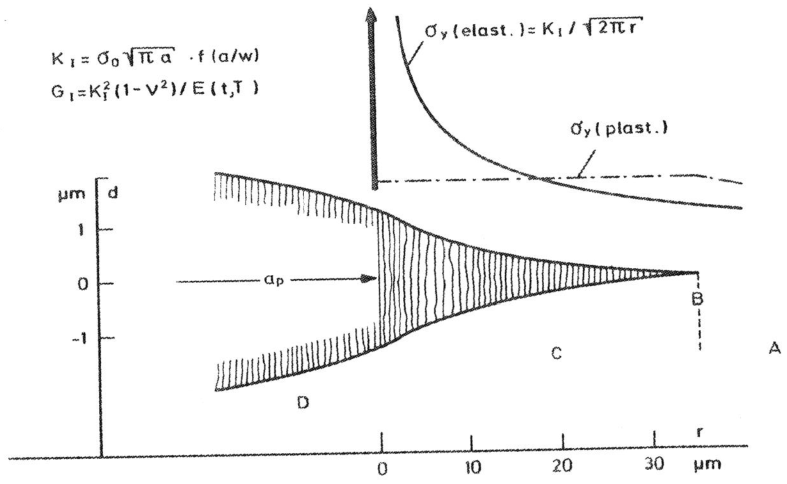


Figure 4 Substructure of highly oriented semicrystalline fibers; polyethylene: before (a) and after (b), annealing treatment (5), 6-polyamide: as drawn (6)



Crack opening in polymers

Figure 5 Homogeneous straining (A), craze initiation (B), non-homogeneous deformation of crazed material (C) ahead of a slowly propagating crack (D) in a glassy polymer (e.g. polymethylmethacrylate, 13)

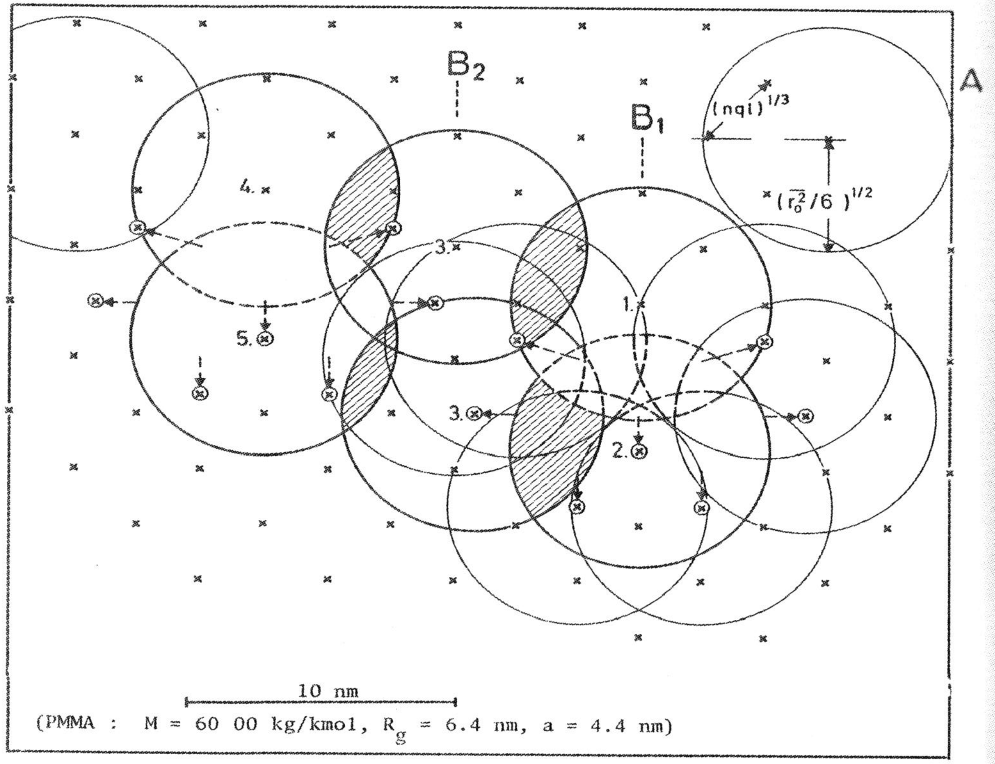


Figure 6 Molecular interpretation of craze initiation:

A Homogeneous response of matrix
B$_1$ Decohesion of non-entangled molecular coils 1 and 2
B$_2$ Anelastic deformation of entangled coils 3; transfer of strain onto other non-entangled coils, e.g. 4 and 5; a fibril will eventually be formed at B$_2$ - it consists of interpenetrating, partially oriented molecular coils