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Yield strength and anelastic limit of amorphous ductile polymers

Part 2 *The model of yield*

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This paper describes a molecular model of yield for glassy polymers using polyethylene as the model material. The derived yield strength is simply related to fundamental molecular properties of the material. The mechanism of yield does not rely on any of the classical dislocation concepts. Instead it is shown that the yield strength of an amorphous glassy polymer should be viewed in terms of the integrity of a network of the strongest intermolecular bonds in a relatively weaker matrix. Furthermore it is shown that amorphous polymers behave in an anelastic manner as a result of their microstructure. The magnitude of the anelastic strain limit for $\sigma = \sigma_y$ is also derived in terms of molecular quantities.

1. Introduction

A characteristic feature of ductile materials is that, when deformed under mechanical forces, they show two distinct regions of behaviour: (i) an initial recoverable "elastic" region; and (ii) a largely non-recoverable "plastic" region. The critical stress at which this change occurs is called the yield strength, and the corresponding strain – the elastic limit. Both are connected to a particular molecular mechanism which leads to the change from elastic to plastic behaviour.

The conceptual introduction of the dislocation by Taylor and Orowan and Polanyi, and its experimental verification by Mitchell and others, created a major landmark on the way of the development of Materials Science. It has had a major influence on the understanding of mechanical behaviour of crystalline materials. In addition, such thinking has led to the formulation of two theories for the yield strength of amorphous polymers [1, 2] which rely wholly or partially on concepts derived from dislocation or disclination theories. However, there are good reasons for not using such essentially crystalline concepts to explain plasticity in amorphous polymers and, indeed, several molecular theories of yield in amorphous polymers, independent of the concept of dislocations, have already been proposed [3–5]. It will be shown in this paper that deformation in, and the yield strength of amorphous polymers should be viewed in terms of the integrity of a network of strongest intermolecular bonds (not the covalent backbone bonds) in a relatively weaker matrix. This is in contrast to the case of ductile metals, in which the strength of a hard matrix (crystal lattice) is determined by a network of weaknesses (dislocations).

2. Assumptions of the model

The development of the model is based on the following premises:

1. Plastic flow is a manifestation of the breaking of atomic bonds under the influence of stress, and must follow the principle that weaker bonds break first.
2. Deformation in amorphous polymers up to the yield point is a fully recoverable, anelastic deformation.
3. The structure of amorphous polymers is that represented by a random packing of molecular chains. This implies a distribution of monomer to monomer distances around the average value as calculated from the density (or the specific volume), and also a distribution of relative orientations of chain segments.
4. Changes of density (or specific volume) with temperature or with microstructure occur by changes in separation of molecular chains only. The length of the chain, i.e. the C–C distance along the backbone and the valency angle remain unaltered (to a first approximation) over the temperature range of interest.
5. Below the glass transition temperature flow in amorphous polymers involves an interdependent motion of segments of the molecular chain, each segment comprising a number of repeat units. The length of the segment, i.e. the number of the repeat units per segment, changes with temperature.
6. Finally, the kinetic effects due to thermal vibrations and the associated molecular transitions, are excluded from this description of the model. It follows that strain-rate effects are also not considered at this stage. However, the implications of these on the model are discussed later on.

The model to be described relies to a major extent on the fact that polymers, unlike metals, show a large variation in density between their respective crystalline and amorphous states. For example, the theoretical density of crystalline polyethylene at room temperature is $1.000\,\mathrm{g\,cm^{-3}}$, whereas the density of a completely amorphous polyethylene is estimated to be $0.875\,\mathrm{g\,cm^{-3}}$. The change, expressed as $\Delta\varrho/\varrho$, is 12%. The corresponding change in density for glassy and

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crystalline alloys, for example, Metglas alloy of Pd–Ni–P is less than 1%. Even on melting of pure metals the change in density from solid to liquid is no more than 3 to 4%. This difference is due, of course, to the high anisotropy (and variety) of atomic bonds which enforce the existence and protect the integrity of the molecular chains. The random packing of the molecular chain encounters different geometrical limitations compared to those imposed on random packing of individual atoms with relatively isotropic metallic bonding, as in metallic glasses.

The next important feature on which the model is based is the assumption as to the distribution of the CH_2 to CH_2 group distances to be found in a randomly packed (amorphous) polyethylene. Whilst definite experimental facts on this aspect are still lacking, one can make a reasonable guess as to the shape of this distribution. For the purpose of the model presented here this distribution is assumed to have a rectangular shape, of width equal to $(r_{\max} - r_0)$ and height equal to N_ϱ, as was derived in Part 1 of this publication [6].

3. The model of yield

The essential features of the model can be derived to a first approximation from the diagram shown in Fig. 1. It is assumed that the deformation of every chain element in the amorphous polyethylene relative to its nearest non-covalent neighbouring segments will be governed by this illustrated force–distance law.

Fig. 1 shows the variation of the potential energy, $U(r)$, and its first derivative, $\partial U(r)/\partial r = f(r)$ against chain separation for two parallel chains of polyethylene. The $U(r)$ curve is drawn on the basis of Lennard–Jones potential [7, 8]. The minimum in potential energy of $-7.69\,\mathrm{kJ\,mol^{-1}}$ is taken from the lattice cohesive energy of polyethylene [9, 10]. The equilibrium separation of 0.46 nm is an average value of chain spacings along (0 1 0) and (1 1 0) directions in the lattice extrapolated to 0 K.

Let us consider the material at a temperature of 213 K. At the points of constriction discussed earlier [6], there will be CH_2–CH_2 non-covalent pairs at their optimum binding distance r_0 with the corresponding maximum binding force $f_{\max}$. To maintain the amorphous density there must be CH_2–CH_2 non-covalent pairs at separations indicated in the diagram as $r_{\max}$ and for that matter, at all spacings in between r_0 and $r_{\max}$.

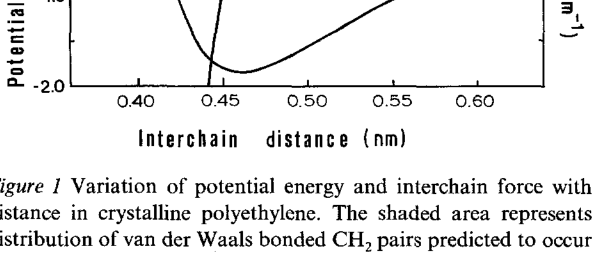

Figure 1 Variation of potential energy and interchain force with distance in crystalline polyethylene. The shaded area represents distribution of van der Waals bonded CH_2 pairs predicted to occur in amorphous polyethylene.

The height of the box, N_ϱ, indicates the number of the CH_2 pairs at a given separation, and the distance from r_0 to $r_{\max}$ indicates the width of this distribution. One can make the observation that some CH_2 pairs are on the fringe of intermolecular interactions, some are arranged at their maximum, and others occupy intermediate positions.

The mechanical behaviour of such a structure is different from the usual picture presented for discussions of the strength of crystalline materials. On application of an external load, the chain segments positioned at $r_{\max}$ will need only a small load to flip over the $\partial U/\partial r = f_{\max}$ peak, contributing immediately to the "plastic" (or more correctly, anelastic) component of deformation. On increased loading this process will continue, i.e. molecules with closer spacing and higher binding force will be dragged over the force–distance peak. Finally, a value of externally applied load will be reached at which breaking will occur of the bonds between those segments which have the maximum binding force.

The collection of all the molecular segments with r_0 spacing and maximum binding force $f_{\max}$ acts as a "memory network" in the amorphous polymer. On removal of load before the critical value the material will anelastically return to its original configuration because the CH_2 pairs with maximum bonding will exert back-pull through the covalent bonds on the "flipped" segments of the chain.

It is now proposed that the strength of this memory network determines the yield strength of the material. Thus to derive the tensile yield strength we refer to Fig. 2. When the applied stress reaches a value such that the memory network in the polymer is just on the point of breaking, then a force of the magnitude $f_{\max}/(\bar{r})^2$ must be applied to each of the CH_2 pairs which constitute the network. Since there are N_ϱ of these pairs, and assuming shear yield criterion, the tensile yield strength of the material must be

$$\sigma_y = \alpha N_\varrho f_{\max}/(\bar{r})^2 \qquad (1)$$

where α includes a geometrical constant (analogous to the Schmidt factor), and Avogadro's number (because of the units of $f_{\max}$). N_ϱ, $f_{\max}$, and $\bar{r}$ were defined previously when discussing Fig. 1. Noting that

$$\varrho_a = \frac{\text{mass}}{\text{volume}} = \frac{\text{mass of }(CH_2)}{(\bar{r})^2 l_{C-C} \sin\theta/2} \qquad (2)$$

where l_{C-C} is the length of covalent C–C link and θ is the C–C–C valency angle. Now $\bar{r}$ can be eliminated from Equation 1 to obtain

$$\sigma_y = \beta N_\varrho f_{\max} \varrho_a \qquad (3)$$

where $\beta = [\alpha l_{C-C} \sin(\theta/2)/(\text{mass of } CH_2 \times \text{Avogadro's number})]$.

This is a totally novel view of the yield process in amorphous polymers, based entirely on a molecular approach. Equation 3 relates the yield strength to

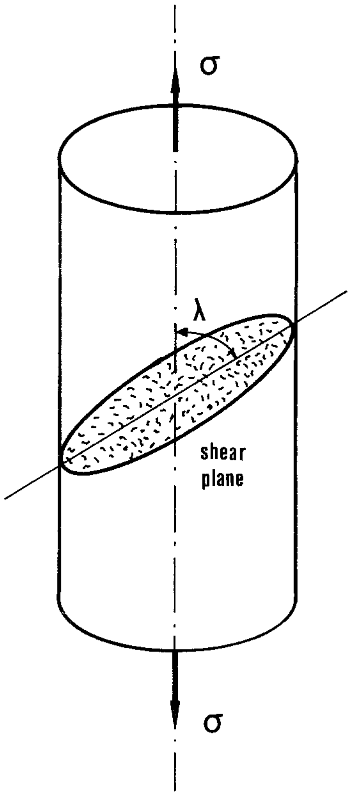

Figure 2 The magnitude of yield stress in simple tension involves Schmidt factor for the resolved shear stress on shear plane.

fundamental material properties. Note that β and $f_{\max}$ are temperature and pressure independent quantities. However, N_ϱ is a function of ϱ_a which depends on both temperature and pressure.

4. Evaluation of N_ϱ

In Part 1 of this paper [6] the structure of amorphous polyethylene was described in some detail. An important feature was the concept of the points of constriction, which effectively divide the length of any chain into segments of, at this stage, an undefined length. In this part of the paper a special function is assigned to these segments as being the elemental unit of the non-conservative motion leading to yielding of the polymer. The value of N_ϱ is in some reciprocal way linked to the length of these segments. No scheme for the calculation of N_ϱ from basic principles is presented at this stage. Instead we proceed to estimate the value of N_ϱ from experimental results on chain motion in solid polyethylene published by Hentschel *et al.* [11].

The chain motion in the amorphous regions in linear polyethylene was studied by using various deuteron n.m.r. pulse methods. The results were analysed in terms of the highly constrained conformational motions in the temperature range from 100 to 300 K. Their work, as well as that of many other similar studies of polyethylene, has shown that on increasing temperature there is found to be an increased fraction of mobile chains in the amorphous regions of polyethylene. More importantly, they were able to show that this mobility is at first (low temp) restricted to segments of the chain of 3 bond lengths, then at higher temperatures 4 to 6 bond chain segments become mobile and at room temperature 7 and longer bond segments acquire this mobility.

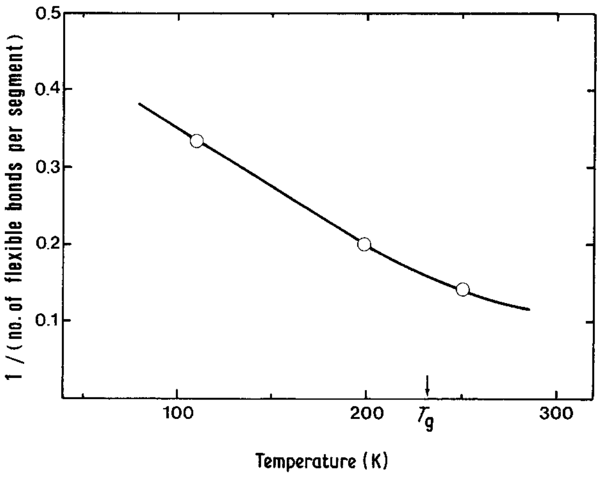

Figure 3 The inverse of the number of flexible bonds per chain segment in polyethylene as a function of temperature – obtained from [11].

Clearly seen here is a connection between the above described mobility and the structure of amorphous polyethylene, as described earlier in this paper. One can identify the *n*-bond segments with the chain segments between the points of constriction. Therefore we define N_ϱ as proportional to $1/n$-bond segment at a given fraction of mobile segments in the bulk of the polymer.

Intuitively we may require that at least one in five of the segments must have the freedom to move (i.e. enough free volume) for the material to yield plastically. Therefore, referring again to the work of Hentschel *et al.* [11], we may plot $1/n$-bond of flexible segments, when that mobility achieves some 20% of the bulk. This plot is shown in Fig. 3.

5. Calculation of the yield strength of amorphous polyethylene

The following data are required in Equation 3

α – assume to be equal to 2

$l_{\text{C-C}} \sin \theta/2 = \frac{1}{2}\, c\text{-axis} = 2.54 \times 10^{-10}\,\text{m}$

mass of $\text{CH}_2 = (12 + 2)\ 1.67 \times 10^{-27}\,\text{kg}$

Avogadro's number $A = 6.02 \times 10^{23}\,\text{mol}^{-1}$

$f_{\max} = 4.6 \times 10^{-10}\,\text{N mol}^{-1}$

$\varrho_a = 1/v_a = 914\,\text{kg m}^{-3}$

The values of N_ϱ are taken from Fig. 3, and the values of ϱ_a are taken from Fig. 1 in the previous paper [6]. Thus finally the plot of the yield strength, σ_y, against temperature, as calculated from Equation 3, is shown in Fig. 4.

The general trend of σ_y with T as predicted by Equation 3 is acceptable, and in agreement with experimentally observed behaviour of amorphous polymers.

6. Calculation of the anelastic limit in amorphous polyethylene

Another feature of the model is that it predicts the strain up to the yield point as a recoverable anelastic deformation. This may be understood as follows.

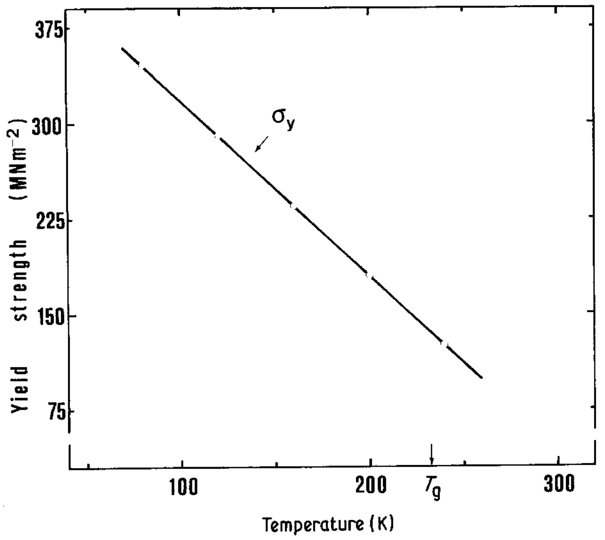

Figure 4 The predicted variation of yield stress with temperature for polyethylene from Equation 3.

In a segment of n-bonds, each CH_2 is distributed equally between r_0 and r_{max}, as implied in Fig. 1. With increasing stress the CH_2 situated closest to f_{max} will flip over – thus contributing immediately to anelastic strain. At a higher stress the next CH_2 nearest to f_{max} will flip. However, if at this stage the load is removed, the CH_2 groups must return to their starting point. This is because they are connected by the covalent bonds to the rest of the segment. The points of constriction at both ends of the segment require force $f = f_{max}$ to be undone, and hence are still holding firmly. Therefore, these remaining parts of the segment will pull back the "plastically deformed" CH_2s over the peak, and back to their original positions. However, since this is a non-conservative motion, on a macroscopic scale this will result in a mechanical hysteresis.

A simple way to calculate the anelastic limit (i.e. the strain at which $\sigma = \sigma_y$ and the points of constriction (memory network) are being broken) is as follows.

To break the memory network the applied stress must be equal to σ_y. The corresponding strain must be such that it moves CH_2 pairs spaced at r_0 to spacing at $r(f = f_{max})$. Therefore

$$\varepsilon_y^{an} = \frac{r_{f_{max}} - r_0}{r_{f_{max}}} \tag{4}$$

In terms of the diagram in Fig. 1, this gives a value of about 6% which agrees very well with the values measured in most amorphous polymers.

7. Discussion

7.1. Prediction of σ_y and ε_y^{an}

In Fig. 4 the yield strength of amorphous polyethylene at 213 K is of the order of $150\,MN\,m^{-2}$. Compared with other amorphous polymers, such as polystyrene or PMMA, this figure seems somewhat high. The yield strength of the latter two polymers is around $50\,MN\,m^{-2}$ at temperatures around 20° C below their T_g. This discrepancy may be viewed in two ways.

The figure of $150\,MN\,m^{-2}$ is close to being correct (but remains to be confirmed experimentally), and reflects the influence of the absolute value of temperature, i.e. 213 K for PE compared with 350 K for PS. This means that the yield strength of PS or PMMA is effectively lowered by thermally activated processes due to the higher temperature involved.

The other view is that the figure of $150\,MN\,m^{-2}$ is inaccurate because the estimation of N_ϱ is very poor. This view may be correct because there is no definite model proposed as yet for the calculation of N_ϱ, and it was obtained by indirect means in the above calculations. In this case the problem still remains to be resolved.

On going to low temperatures, N_ϱ tends to the value of 1, and correspondingly σ_y ought to approach the theoretical shear strength of polyethylene on the crystallographic $\{1\,1\,0\}$ plane. The simplest calculation of the theoretical shear stress of a crystal was proposed by Frenkel [12] and discussed by Kelly [13]. The shear modulus G for the $\{1\,1\,0\}$ plane in polyethylene is $6\,GN\,m^{-2}$ at 170 K. Taking $\tau_{max}/G = 1/10$, we find $\tau_{max} = 600\,MN\,m^{-2}$, which must be considered as the upper limit for σ_y at low temperatures.

An important feature of the above model is the prediction of the "anelastic limit", i.e. the recoverable strain at the point of yield. This is in contrast to crystalline materials, from which we define the "elastic limit" at the point of yield. In both cases the deformation of the material is recoverable for all $\sigma < \sigma_y$, but in the case of amorphous polymers the deformation is time dependent and hysteretic. Thus the model predicts anelasticity and hysteresis as an integral part of the yield process, and not incidental to it through thermally activated jumps. However the anelastic strain is fully recoverable only if $T > 0\,K$ as the elastic strain energy stored in the material is insufficient to restore original positions of all atoms.

The value of ε_y^{an} as predicted by Equation 4 is of the right order of magnitude since most amorphous polymers show yield at strains between 5 to 10%.

7.2. Other yield theories

One of the earliest theories of flow in polymers was proposed by Eyring [3]. A significant contribution of Eyring's work is the concept of configurational space of potential energy, in which forces between the atoms are equal to the gradient of the surface at any point with respect to distance. It is recognized that molecular models of yield and flow cannot successfully represent the atomic movements unless the configurational surface is explicitly known. This point was emphasised by Argon and Bessonov [14] in their paper on plastic flow in glassy polymers.

The potential energy curve from Fig. 1 represents a trace of the cross-section between the configurational surface around any CH_2 group and a plane of motion of that particular group in the amorphous polyethylene. This represents a small portion only of the total surface. A more complete surface is illustrated in Fig. 5 where, under the applied forces, the B molecule is moved to the right, away from molecule A. The initial distance between A and B is taken as $r_0 = 0.46\,nm$. To break the van der Waals bonding between A and B, it is necessary to move B by the distance

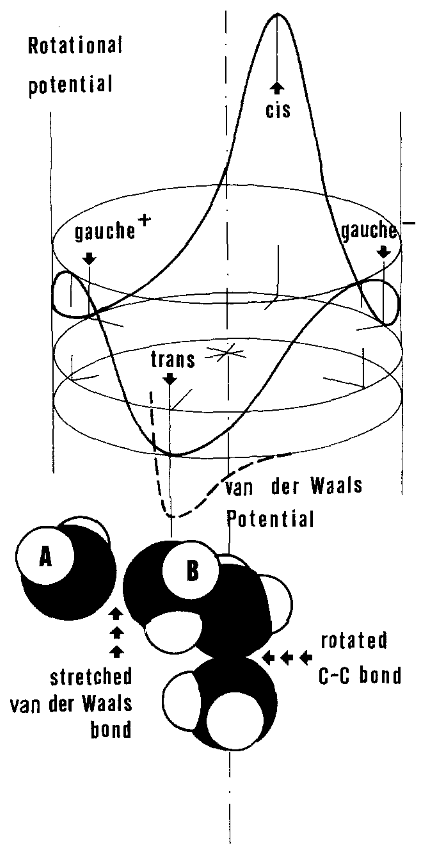

Figure 5 Variation of potential energy for rotation around the covalent carbon–carbon bond and van der Waals interaction between A and B CH_2 groups.

$[r(f = f_{max}) - r_0]$, i.e. about 0.05 nm. Of course B can move only along a circular path, and in this motion will sweep an angle of about 20°, which is insufficient to move it into the gauche position.

A somewhat similar approach was adopted by Yannas [5]. However, the use of continuum mechanical concepts to calculate the required torque on a strophon to make it yield conceals the molecular nature of this process.

The theory of yield proposed by Robertson [4] relied entirely on the rotational potential. Later work by Haward *et al.* [15] showed that rotational transitions indeed may play a role at larger plastic strains, and lead to strain hardening. However, it must be concluded that the Robertson theory cannot be applicable to the onset of yield in polyethylene which occurs for strains between 5 to 10%.

7.3. Dependence on temperature and hydrostatic pressure

The yield strength σ_y is related to temperature through the parameters N_ϱ and ϱ_A.

The variation of N_ϱ and ϱ_A with temperature is a manifestation of the changes in spacings between the van der Waals bonded CH_2 pairs. As the temperature drops down, the difference between $\bar{r}$ and r_0 (as in Fig. 1) must reduce. Consequently the width of the distribution must decrease, and its height, N_ϱ, will increase in some fashion consistent with the overall changes in density. The change in resistance to deformation of the material at different temperatures is therefore a reflection of the restructuring in the CH_2-pairs distribution function with temperature.

Hydrostatic pressure must have a direct bearing on the value of yield strength, again through its effect on the density of the polymer. The change in spacings between CH_2-pairs is related to the changes in density or specific volume by

$$\Delta r/r_0 = \tfrac{1}{2}\Delta\varrho/\varrho = \tfrac{1}{2}\Delta V/V \qquad (5)$$

Consider the constitutive equation

$$p_h = K(\Delta V/V) \qquad (6)$$

where p_h is the hydrostatic pressure and K is the bulk modulus. Substitution of Equation 6 in 5, and 5 in 1 leads to

$$\sigma_y = \alpha N_\varrho f_{max}/[r_0(1 + p_h/2K)]^2 \qquad (7)$$

If the tensile yield strength is measured at both an atmospheric pressure and a superimposed hydrostatic pressure, then to a first approximation the ratio of these two is given by

$$\sigma_y^h/\sigma_y^{atm} \cong 1/(1 - p_h/K) \qquad (8)$$

The yield strength of polycarbonate at room temperature and atmospheric pressure was measured at 33 MN m^{-2}, and that measured under hydrostatic pressure p_h = 450 MPa was around 60 MN m^{-2} [16]. If the bulk modulus K is taken to be around 1000 MN m^{-2}, then putting these values in Equation 8 predicts very closely the ratio derived from the experimental data.

7.4. Comparison with yield in crystalline materials

In crystalline materials Young's modulus and yield strength are essentially independent material properties. The modulus of elasticity is the property of the crystal lattice, whereas the yield strength is a function of lattice defects, and its value may be varied by as much as two orders of magnitude without changing the modulus. But, if the defects can be eliminated (or made ineffective) then modulus and strength are closely related through theoretical strength calculations.

In polymeric materials Young's modulus and yield strength are more a property of the molecule rather than that of the crystal lattice. Therefore, both the modulus and strength are varied together by changes in microstructure (i.e. preferred molecular orientation). In a general sense this applies also to amorphous polymers. Clearly, the theory of yield for amorphous polymers should not, therefore, contain any elastic modulus as one of the independent variables.

However, one analogy with crystalline materials can be made. The distribution in bond strength (Fig. 1) can be viewed as analogous to a variety of dislocations with different Burgers vectors. The dislocations with least Burgers vector (smallest Peierls–Nabarro force) correspond to CH_2–CH_2 pairs with least van der Waals bonding (i.e. separation r_{max}). Next some CH_2–CH_2 pairs with greater bonding correspond to dislocations requiring greater force to move, and so on. For example, in bcc iron dislocation activity occurs well below yield point – the latter occurring only when the major network of dislocations breaks away from their locking atmospheres. Thus, in amorphous polymers flipping of CH_2 groups over f_{max} occurs well below σ_y. However, the yield strength is reached only when the stress is sufficient to break the "memory network" formed by the chain molecules in the bulk of the polymer.

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