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Yield strength and anelastic limit of amorphous ductile polymers

Part 1 *Amorphous structure and deformation*

Z. H. STACHURSKI
Department of Materials Engineering, Monash University, Melbourne 3168, Australia

The microstructure of amorphous polyethylene below its glass transition temperature is described in some detail. The dimensions, shape and statistical mechanics of a polyethylene chain are already well understood. The packing of such molecular chains is less understood and it is considered here in terms of a CH_2 pair distribution function. The pair distribution function is derived on the basis of (i) the variation of specific volume with temperature for completely amorphous and ideally crystalline polyethylene, and (ii) randomness of packing of the molecular chains. A scheme for the description of deformation of amorphous polymers is proposed. Points of constriction along the molecular chain are defined in terms of variation of cross-sectional area of the molecular tube. During deformation the points of constriction are convected with the body of the polymer. However, the deformation of the chain segment between the points of constriction is analysed in terms of kinematics of chain linkages.

1. Introduction

The process of yield involves breaking and reconstituting atomic bonds. In order to be able to say anything sensible about this process it is necessary to understand; (i) the amorphous microstructure of the material on a molecular level, and (ii) the existing hierarchy of the atomic bonds.

A detailed knowledge of the amorphous microstructure in polymers below the glass transition temperature is not generally available. Perhaps the best described microstructure of a glassy polymer is that of atactic polystyrene [1]. Some, albeit incomplete, knowledge about other amorphous polymers also exists [2, 3]. In this paper polyethylene is chosen as the model material of an amorphous polymer for the description of the yield process below the glass transition temperature. Since a completely amorphous polyethylene is difficult to obtain experimentally below its glass transition, this choice requires some explanation and justification.

For the purpose of the model of yield presented in this paper the most desirable feature in the polymer is the simplicity and uniformity of its molecular structure. This is exemplified by linear polymers with the most basic repeat units such as polyethylene, polytetrafluoroethylene, amorphous sulphur, selenium, and others. Of these, polyethylene is the most thoroughly studied polymer; i.e. the type and strength of the atomic interactions is well established [4–11]. The statistical conformations of the polyethylene chain have been worked out theoretically [12], and confirmed experimentally [13, 14]. The relevant physical properties, thermodynamic data and the glass transition temperature are known [15, 16]. On the basis of all this information it is possible to describe and visualize the amorphous structure of polyethylene below its glass transition temperature with a high degree of confidence. Thus point (i), as stated in the first paragraph, can be satisfied.

As regards point (ii), Wunderlich [16] lists the energy associated with chemical bonds in polymers in the following general order:

1. Covalent bonds (order of magnitude 420 kJ mol^{-1} of bonds).
2. The next biggest contribution comes from the change of potential energy on rotation (approximately 4 to 50 kJ mol^{-1}).
3. The next contribution is from interactions due to hydrogen bonds or dipoles (usually between 4 and 40 kJ mol^{-1}).
4. Finally the van der Waals dispersion bonds (around 0.4 to 2 kJ mol^{-1}).

Thus the first manifestations of mechanical yield in polyethylene (in which bonds of type 3 are absent) should occur at stress levels which are just sufficient to break the weakest type, i.e. van der Waals interchain bonds. However, it is important to point out that with increasing deformation strain-hardening due to entanglement may take place. This will increase the stress level, and consequently cause breaking of the next weakest bond, i.e. rotation around the covalent C–C bond [17].

Several molecular theories for yield in amorphous polymers have been proposed [18–22] and are reviewed in Part 2 [23]. In contrast to these theories the model presented in Part 2 of this publication places the responsibility for the onset of yield in amorphous polyethylene on the breaking of the interchain van der Waals bonds [23]. There seem to be two general arguments supporting this view.

Firstly the interchain bonds are the weakest of all

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bonds in this structure, and this satisfies the principle that the weakest link should determine the strength.

Secondly, at the strain levels at which yield in amorphous polymers is observed (i.e. around 5 to 10%), the deformation of the molecular chain does not necessitate the drastic trans to gauche or gauche to trans rotations, as is required by some of the above mentioned theories. Both of these arguments are developed fully in this paper.

2. The structure of amorphous polyethylene below T_g

It is customary to assign van der Waals radii to the atoms, and represent the molecules by a so-called hard-sphere model. In the case of covalent bonding the spheres of the atoms defined by the van der Waals radii, are thought to interpenetrate to distances usually close to the sum of the covalent radii.

The van der Waals radius for the carbon atom is 0.170 nm, and that for the hydrogen atom is 0.117 nm. In a repeat unit of polyethylene, $-[CH_2]-$, the C–H distance is only 0.109 nm due to the strong covalent binding forces between these two atoms. The $[CH_2]$ group is the smallest building block of the polyethylene chain [16].

The C–C covalent bond along the molecular chain fixes the separation of the repeat units at a distance $l_{c-c} = 0.154$ nm, and adjacent bonds form an angle of 109.5°. The H–C–H angle on each repeat unit is about 107°, and a plane on which these three atoms lie, bisects the C–C–C angle. The molecular parameters listed so far vary little with temperature or normal levels of mechanical stress, and henceforth will be considered as constant.

As is well known, the isomerism of a molecular chain arises from rotations around the covalent C–C bonds, with preferred positions named trans (t), gauche$^+$ (g^+) and gauche$^-$ (g^-). The flexibility of the chain leads to random coil configurations. In equilibrium the random configurations of the chain have a common feature, namely the so-called end-to-end distance

$$\bar{L} = 0.218(N)^{1/2}C_\infty \quad \text{(nm)} \qquad (1)$$

where N is the number of repeat units in the chain, and C_∞ is the characteristic ratio [12] which embodies the statistical mechanics of real chains. The value of C_∞ for polyethylene at a temperature of 413 K (melt) is equal to 6.8, as calculated by Abe *et al.* [24], and confirmed experimentally by Schelten *et al.* [14]. Thus two polyethylene chains with the same number of repeat units will assume the shapes of two different random coils, but will have the same end-to-end distance, the same overall ratio of trans to gauche bonds, and the same thermodynamic potential [16].

The packing of such molecular chains of polyethylene at a temperature of 413 K (140° C) has been studied by many workers [14, 25–28], some holding the view that short order must exist in amorphous polymers. However, accumulated experimental evidence and careful analyses point to the fact that true amorphism does exist in, at least, the molten state of polymers [27, 28]. In particular Lovell *et al.* [28] concluded that the amorphous structure of polyethylene can be best represented as an assemblage of random chains with uncorrelated segments distributed as closed packed random spheres.

It is reasonable to expect that, if the polyethylene melt were quenched from 413 K to some suitably chosen low temperature so rapidly as to prevent any crystallization, then the amorphous structure would be retained in the supercooled polymer. There is sufficient experimental evidence for that happening in other polymers [29].

It is assumed that the glass transition of amorphous polyethylene is 237 K [15]. In oder to prevent crystallization and to retain the supercooled structure let us consider this material to have been quenched to 213 K (some 20 K below T_g). The configurations of the individual chains will be "frozen-in". Therefore, all trans and gauche conformations and the end-to-end distances will remain, at least initially, the same as in the melt. However, the volume of the polymer will be diminished, as shown in Fig. 1. This decrease in volume is accounted for by a decrease in spacings of the non-covalently bonded repeat units only. Now it is necessary to discuss the packing of the chains in the solid polyethylene in greater detail. The case of the crystalline polyethylene is described first as the basis for evaluation of the amorphous structure.

In crystalline polyethylene the chains form a close-packed orthorhombic crystal with lattice constants a, b and c. Two chains comprise the crystallographic repeat unit; one in the corner and one in the centre of the cell. An accurate measurement of the unit cell dimensions was published recently [30]. The magnitudes of the a and b lattice constants are such that the packing may also be viewed as pseudo-hexagonal, i.e. with a small distortion of the hexagonal base. In this view there are four chains at a distance $= 1/2\,d_{110}$, and two chains at a distance equal to b from the chain at the centre (noting that $d_{110}^2 = a^2 + b^2$). On the basis of the published data we find that at 213 K, $a = 0.733$ nm and $b = 0.493$ nm, hence $1/2\,d_{110} = 0.442\text{ nm} < b$.

The simplest approximation for packing of polyethylene chains is a close-packed hexagonal structure of straight cylindrical rods, with the distance between the centres of the rods $= \bar{d}$. If the density of packing between the orthorhombic and hexagonal structures is to be the same, then it is easily found that $\bar{d} = [ab/(3)^{1/2}]^{1/2}$, and equals 0.457 nm at 213 K.

Let us assume that in the amorphous polyethylene the average spacing between the non-covalently bonded CH_2 pairs is $\bar{r}$. It is of interest to find out what is the value of $\bar{r}$, if the packing in the crystalline material (at the same temperature) is characterized by $\bar{d}$. Noting that the three-dimensional changes in volume must be related to the two-dimensional changes in spacing between chains one obtains: $\bar{r} = \bar{d}/(1 - 1/2\,\Delta v/v_c)$, where $\Delta v = v_a - v_c$, and v_a and v_c are the specific volumes of the amorphous and crystalline polyethylene, respectively. At 213 K $v_a = 1.094 \times 10^{-3}\,m^3\,kg^{-1}$ and $v_c = 0.985 \times 10^{-3}\,m^3\,kg^{-1}$, hence $\bar{r} = 0.483$ nm. Alternatively one can use the relationship that the quantity of mass per unit

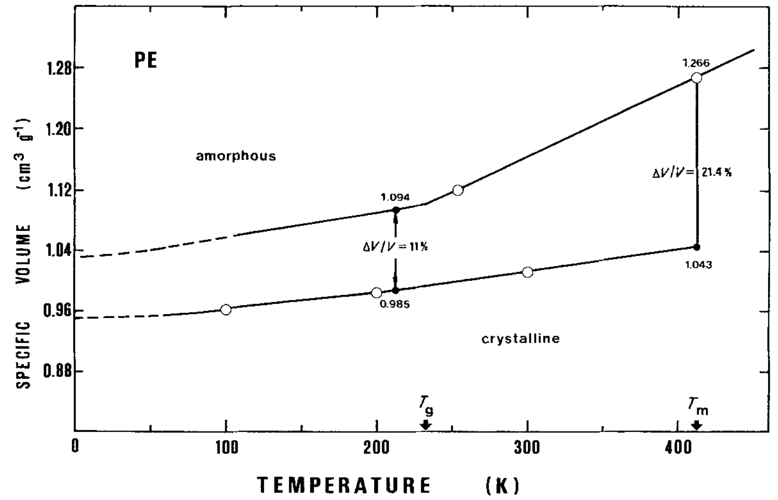

Figure 1 Volume–temperature relationship for ideal amorphous and crystalline polyethylene drawn on the basis of data from [16, 28, 30].

length of chain must be the same in both cases, and therefore obtain $\bar{r} = \bar{d}(v_a/v_c)^{1/2} = 0.481\,\text{nm}$ at 213 K.

Both of the above relations predict an average non-covalent CH_2 to CH_2 spacing in the amorphous polyethylene relative to its crystalline state. These relations satisfy the principle of conservation of mass, but give no indication as to the relative local orientation of the chains or the variation in spacings of the non-covalent CH_2 pairs.

A more specific and precise way to describe the packing of the molecular structure is to define a pair distribution function for the CH_2 groups around an arbitrarily chosen repeat unit in the bulk of the material [31]. For the crystalline material, with the full knowledge of its crystallography, it is possible to calculate the pair distribution function quite precisely. This shown in Fig. 2, up to a radius of 0.516 nm. The next nearest position of a CH_2 group is some 0.05 nm further away, therefore the radius of 0.516 nm is a convenient point at which to limit the function. The concentration of the CH_2 groups rises sharply in the range between 0.4 to 0.5 nm due to the presence of CH_2 groups from the neighbouring chains. In total there are 25 CH_2 groups within a sphere of radius = 0.516 nm (more precisely; 25 centres of CH_2 groups, taking the centre of the carbon atom as the centre of the group). The mass of one CH_2 group is $(12 + 2)\ 1.67 \times 10^{-27}\,\text{kg} = 23.38 \times 10^{-27}\,\text{kg}$. Dividing the volume of the sphere by the total mass gives calculated value of specific volume equal to $0.985 \times 10^{-3}\,\text{m}^3\,\text{kg}^{-1}$. By comparison, the specific volume calculated on the basis of measured unit cell dimensions (as in Fig. 1) is $v_c = 0.985 \times 10^{-3}\,\text{m}^3\,\text{kg}^{-1}$. The agreement is fortuitous, but useful, because similar calculations performed on the amorphous pair distribution function should therefore give the value $v_a = 1.094 \times 10^{-3}\,\text{m}^3\,\text{kg}^{-1}$ (again from Fig. 1). However, in this case the value of v_a is used instead to calculate the number of CH_2s within the sphere of radius 0.516 nm; the result being 22.5. This number is divided between CH_2s on the same chain, and those packed randomly around the central one at the average distance $\bar{r}$ calculated earlier as equal to around 0.48 nm. These CH_2s form a distribution of their own, which in this paper is assumed to have the rectangular box shape as shown in Fig. 2. However, the derivation of the amorphous pair distribution function must be explained in greater detail.

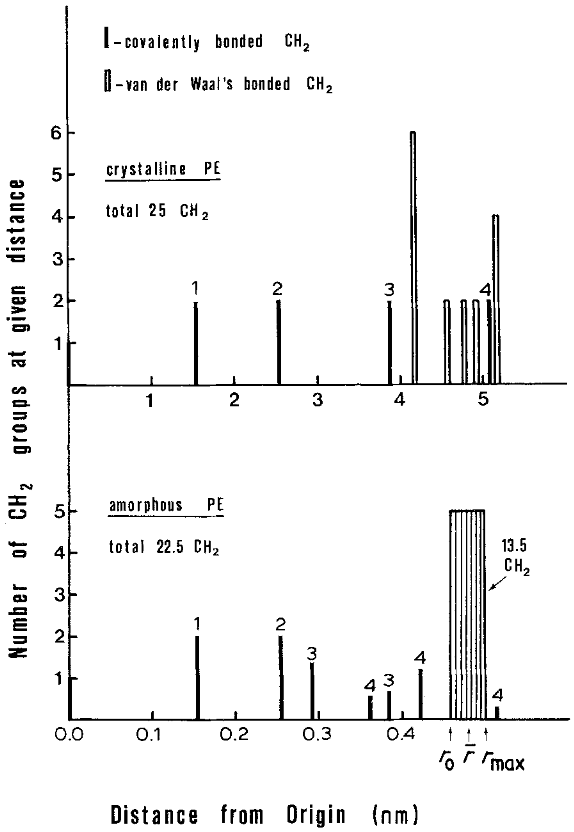

Figure 2 Pair distribution function for crystalline and amorphous polyethylene at 213 K.

In polyethylene the next nearest neighbours to any CH_2 group are always two (one on each side) covalently bonded CH_2 groups, at a distance of 0.154 nm from the CH_2 group at the origin. The second nearest neighbours are again two CH_2 groups, covalently bonded to the first nearest neighbours and found always at a distance of 0.254 nm from the origin. Whilst this distance is fixed, their precise location depends on the trans or gauche configurations of the first covalent bond. The third next nearest covalently bonded CH_2 groups are no longer at a fixed distance from the origin . Their position depends on the configuration of the C–C bond between the first and second neighbour, i.e. trans, gauche$^+$ or gauche$^-$. If it is trans, then the distance from the origin is the same as in the crystalline material (~ 0.39 nm). If it is gauche (+ or −), then the distance is close to 0.292 nm. Disregarding the differences in free energy, the occupation of the former sites will be $1/3 \times 2 = 0.67$, and the occupation of the latter sites will be $2/3 \times 2 = 1.33$, as shown by the relative bar heights in Fig. 2. The fourth next nearest covalently bonded CH_2 groups will be found at three different distances from the origin, characterized by the bond sequences: (i) ttt; (ii) $tg^+t = tg^-t = ttg^+ = ttg^-$; and (iii) $tg^+g^+ = tg^-g^-$ (the $tg^+g^- = tg^-g^+$ sequences are forbidden due to molecular overlap [12]). The occupation/distance will be $(1/7 \times 2)/0.508$ nm $(4/7 \times 2)/0.421$ nm, and $(2/7 \times 2)/0.359$ nm for the three cases, respectively. It is interesting to note that the possible spatial positions of up to the seventh nearest covalently bonded neighbour have been discussed in an early publication [32].

It is now assumed that all other nearest neighbours (regardless of whether they are a part of the same chain, or are from other chains) fall within the rectangular box centred around $\bar{r} = 0.48$ nm. Since the packing of the chains is random we assume equal probability of occupation by the 13.5 CH_2 groups within that box distribution. The width of this distribution is determined by $r_0 \simeq 0.46$ nm which is the closest approach of chains in the crystalline lattice, and $r_{max} \simeq 0.5$ nm which is the expected widest separation on the basis of a box-shaped distribution symmetrical around $\bar{r}$. This completes the description of the pair distribution function of amorphous polyethylene as shown in Fig. 2, and summarizes the understanding of the microstructure of this material.

3. Behaviour under deformation

Consider an element of volume of the polymer with reference to a set of co-ordinate axes XYZ as shown in Fig. 3.

A homogemeoug simple shear is now applied to the volume of polymer in the X-direction and on the XZ plane. To analyse the deformation we imagine two planes parallel to $X-Y$, traversing through the molecules, and separated by an arbitrary distance h. Further analysis will be focused on the deformation of the material (segments of molecular chains) contained between the two imaginary planes of shear.

The phenomenological approach to the description of infinitesimal and finite strain in materials is a classical and fully developed subject and will not be discussed here.

In a molecular approach the deformation of a random coil macromolecule has been treated in great detail in connection with rubber elasticity and statistical mechanics of isomerism. These, however, concentrate mainly on the behaviour of the molecular chain above the glass transition temperature or in solution or in the melt. Here the emphasis is placed on the deformational behaviour of the molecule in an amorphous polymer below its glass transition temperature, and its relationship to the macroscopic deformation experienced by the whole volume of the polymer.

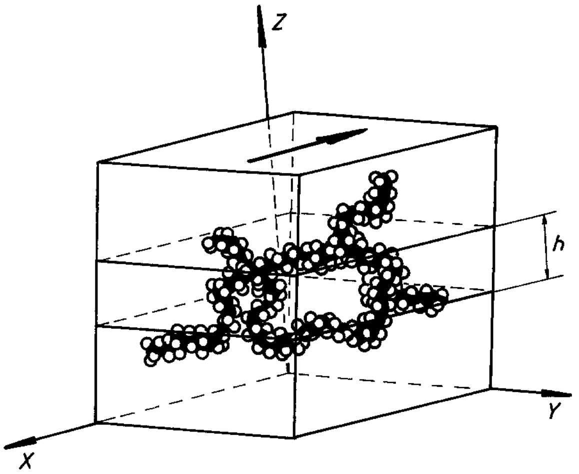

Figure 3 An element of volume of polymer subjected to simple shear deformation. Analysis is focused on the deformation of segments of molecular chains contained between two imaginary planes of shear.

The molecular chain is frequently represented as a series of linkages of length l, angle θ between adjacent links, and free rotation around each C–C bond. This is a very restrictive representation in the sense that it does not allow any changes in l or θ which are expected to occur in the real molecules. Such a chain can be modelled by a series of mechanical linkages with hinges, as shown in Fig. 4.

Several studies of the deformation of polymeric chains in relation to plastic flow have been published [20, 22, 23]. In particular a strophon, defined as a chain sequence comprising a number of rigid segments joined to other strophons by bonds of free rotation, was described as the unit of molecular deformation in polymers. Experimental mechanical models were used to find the most probable number of rigid segments which can be displaced by cooperative rotational motions. In here a different approach is taken. The motions of the chain are considered in terms of an externally imposed general displacement. Indeed the following question is posed; what is the minimum

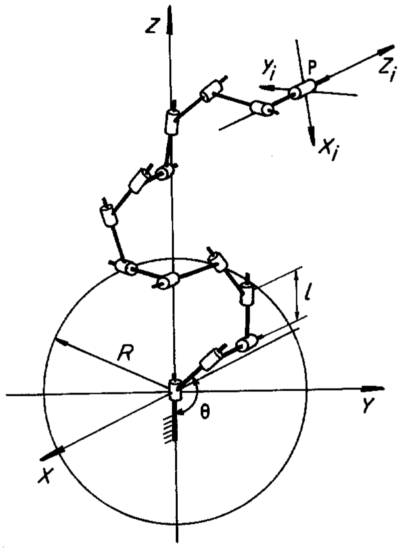

Figure 4 The molecular chain can be represented as a series of mechanical linkages with hinges. What is the minimum number of linkages so that point P can be moved to any point inside the sphere?

number of links in the chain, or chain segment, such that the end of the chain, denoted by P in Fig. 4, can be moved to anywhere within a sphere of radius R centred around the origin? The underlying motivation for this line of thought is as follows: if the end of the chain can be moved to any point inside the sphere, then it means that such a chain can be subjected to any general deformation (of limited magnitude). Intuitively one feels that the above requirements can be satisfied if the chain contains a sufficiently large number of links, and the sphere is sufficiently small. However, it is important to know what is the minimum number of links to fulfill this condition. This would then correspond to a shortest segment of the molecular chain which can be deformed by simple shear within the body of the polymer without straining the covalent bonds.

The kinematics of chain linkages is a subject of its own in the field of mechanics [34]. The analysis of linkages requires co-ordinate transformations around a closed chain which must satisfy the following relationship for each and every configuration

$$[T_{n1}] \ldots [T_{34}]\,[T_{23}]\,[T_{12}] = [1] \qquad (2)$$

where $[T_{i,i+1}]$ transforms coordinates of a point P in i system to its co-ordinates in $i + 1$ system. A full analysis of a chain model based on polyethylene is very involved, and will be the subject of a separate publication. Suffice it to say at this stage that a chain segment of between 7 to 10 links can be shown to satisfy the condition for general deformation, providing the end of the chain P is confined to move in certain portions of the sphere rather than the whole [35]. The exact number of the linkages is not important at this point. What matters is the fact that, given such a segment, it can be deformed freely relying on rotations around the C–C bond only. If the restrictions on the model are relaxed by allowing limited variations $\Delta\theta$ of the angle θ, then movement of the chain becomes freer, and consequently the minimum length of the chain segment will be reduced. In polyethylene the compliances related to bending and stretching of the covalent bonds are about an order of magnitude smaller than the compliance for rotation around the bond. Nevertheless small changes can be expected to occur [12], and a general conclusion can be reached that polyethylene chains possess a high degree of flexibility.

The conceptual aid of the "molecular tube", invented by Doi and Edwards [36] and used so successfully by de Gene to describe reptation [37], is also very helpful in visualizing the deformational behaviour of a molecular chain in an amorphous polymer below its glass transition temperature. The tube is simply the space created around any one molecular chain by the segments of all its nearest neighbouring chains (see Fig. 5).

Due to the randomness of the structure the shape and cross-sectional area of the tube must vary along its length, widening in some places, and coming to minimum dimensions at other points. These latter points will act as constrictions on the molecular chain within, restricting local motions of the chain at these locations. The number of these points of constriction per molecular chain is not evaluated at this stage, but it is clearly directly related to the density of the polymer, and ultimately must have an effect on the macroscopic behaviour of the polymer.

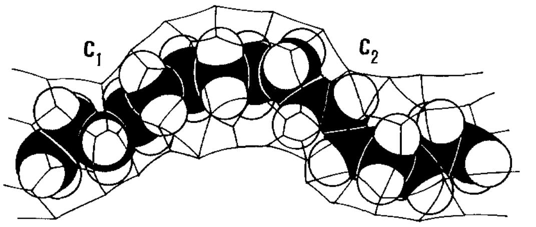

Figure 5 The molecular tube – an imaginary surface dividing the space around any molecular chain from its neighbours. Points C_1 and C_2 illustrate two points of constriction in the molecular tube.

It is assumed that during deformation the points of constriction are convected with the body of the polymer, and experience displacements identical to those of the whole volume of the polymer. However, the displacements of the individual repeat units in the segments of the molecular chain within the tube and between the constricting points will, on average, be different. This can be understood as follows. In an amorphous polymer at the molecular level the material is inhomogeneous. The local configuration and symmetry (if any) of the potential energy phase space is different for each repeat unit (CH_2 group). The freedom of deformation of each repeat unit is (i) severely restricted by the chain-like nature of the macromolecule, and (ii) is strongly affected by the local variations in packing density (free volume). Therefore, under uniform macroscopic deformation the displacements of individual repeat units must be different.

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