The Yield of Polyethylene

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ABSTRACT

Structural changes in polyethylene during annealing have
been characterized by differential scanning calorimetry
traces and the yield point has been examined in plane strain
compression. Analysis of the results suggests that yield is
an activated rate process in which only the pre-exponential
factor changes on annealing.

INTRODUCTION

A considerable amount of work has been performed on drawn and
oriented linear polyethylene to correlate the morphological changes
with the draw ratio. Much of this work has been recently discussed
by Peterlin [1]. Somewhat less has been achieved in clearly de-
fining those factors of structure and deformation processes which
define the yield stress. True stress-strain curves indicate a con-
tinuous change from an initially isotropic material, through yield, to
the drawn fiber. However, only the initial spherulite deformation
from a sphere into a spheroid is uniform [2]. Deformation there-
after is localized in the form of phase changes and twinning and then
chain tilt and slip to produce yield and large-scale plastic deformation
[3]. The stress-strain curve provides a specimen average of these

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discontinuous processes that masks their localized origins. The
factors which control the yield point are those which allow chain tilt
and slip to occur and these are amenable to rate process analysis.
   Two approaches to such analysis are possible. Zhurkov [4] has
shown that the strength of some 50 materials, including many
polymers, is "a time process where rate is determined by mechanical
stress σ and temperature T" and could be expressed as Eq. (1), where

$$t = t_0 \exp[(U_0 - \gamma\sigma)/kT] \qquad (1)$$

"U_0 is the energy barrier determining the probability of breakage of
bonds responsible for strength," t the time to failure, and t_0 and γ
constants. The problem arising in such a technique of fitting empirical
equations to experimental results is the identification of coefficients
with their corresponding physical processes. An alternative approach
is to establish a simplified model for deformation based on known de-
formation behavior. This simple model can be analyzed, predictions
made to check its validity, and if the model is apparently justified
conclusions may be drawn about the values of the coefficients and
their significance.
   Such a procedure has been adopted on the basis of a model proposed
by Cherry and Holmes [5]. The model of a semicrystalline polymer
under the influence of an applied shear stress assumed instantaneous
elastic deformation by the bending of bond angles within the polymer
and concurrent plastic slip within the crystalline regions, stretching
the interfibrillar tie molecules until they break. Failure of the
specimen occurs at a critical rate of chain scission [6]. The plastic
slip is assumed to be facilitated by dislocations within the crystalline
regions of the polymer on those planes favorably oriented to the
applied stress. Dislocations of Burgers vector b and length 1 move
by overcoming an energy barrier ϵ_0 by means of an activated rate
process under the influence of a shear stress τ_p to produce a plastic
shear rate given by

$$\gamma_p = (\rho\beta kT/hl) \exp(-\epsilon_0/kT) \exp(\beta\tau_p/2kT) \qquad (2)$$

where $\beta = b^2 l$ and ρ the density of dislocations.
   The stretched interfibrillar tie molecules fail, according to the
Reiner-Weissenberg failure criterion [7], when the strain reaches
a critical value given by $\gamma_c = (2R/G_e)^{\frac{1}{2}}$, where G_e is the effective
elastic modulus of the network. The failure stress is then given
by

$$\tau_f = (2kT/\beta) \ln j + (2kT/\beta) \ln (hl/\rho\beta kT) + 2\epsilon_o/\beta + (2RG_e)^{\frac{1}{2}} \quad (3)$$

Then, for a constant strain rate experiment, a log/linear relation between strain rate and strength is predicted since the last three terms on the right-hand side are constant at a given temperature.

The mechanical testing to be described here is an extension of the work performed in shear by Cherry and Holmes. This work seeks to examine the dependence of the parameters occurring in Eq. (3) upon the structure of the polymer. To this end, the structure of the polymer is varied by a heat treatment procedure and the effect upon mechanical properties is examined.

EXPERIMENTAL

Sample Preparation

Branched polyethylene (approximate 30 methyl groups per 1000 C atoms) of density 0.918 g/cc was used in this work, supplied by ICIANZ and coded WNC18. It was found to be necessary to maintain close control over all stages of processing and annealing of the polymer to achieve reproducible results. Granules of the polymer were milled at $100°C$ for 3 min to obtain a homogeneous composition. A 7-in. square sheet 1/8 in. thick was compression molded at $180°C$ for 10 min and cooled to $25°C$ by running water through the platens of the press. It was then annealed at some temperature in the range $90-105°C$ for 10 min prior to cooling as before to $25°C$. The temperature was controlled to $\pm\frac{1}{4}C°$ and the temperature variation across the sheet was less than $\frac{1}{2}C°$. Strips $2\frac{1}{2}$ in. wide for mechanical testing were cut from the sheet with a thickness variation of not more than ±0.001 in. about a mean value. Samples of 2 to 5 mg for calorimetric tests could be taken from the same sheet. Subsequent experiments were carried out on material aged at room temperature for approximately 24 hr.

Differential Scanning Calorimetry

A preliminary investigation of the structure of molded and annealed samples of polyethylene was made by a differential scanning calorimetry (DSC) technique. A Perkin-Elmer DSC-1B was used to record the fusion endotherm which has a shape characteristic of the structure of the sample.

The resulting endotherms for samples which had been annealed at various temperatures just below the melting point are shown in
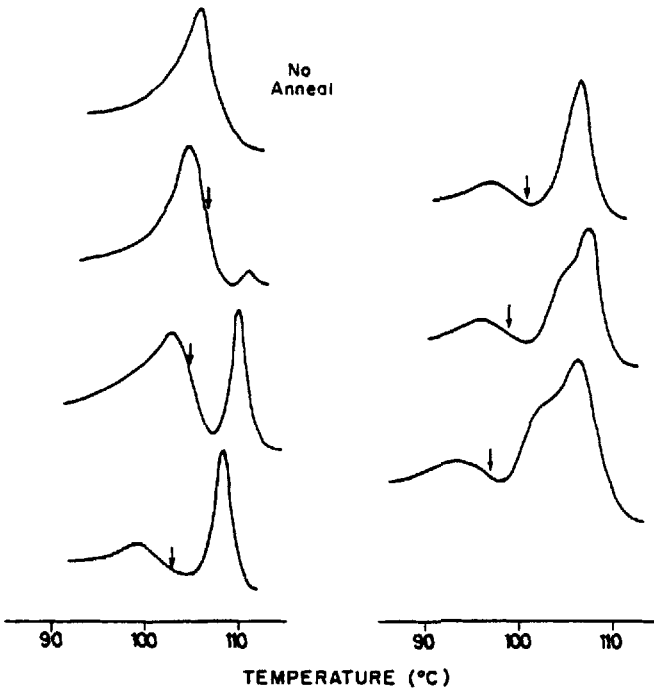
FIG. 1. DSC endotherms for unannealed and annealed samples of low-density polyethylene. Samples were annealed for 10 min at the temperature indicated by the arrow.

Fig. 1 and may be compared with one which has undergone the molding cycle only with no subsequent anneal. This latter endotherm may be interpreted as suggesting that prior to annealing there exists a range of crystallite forms with a range of melting temperatures. The rapid cooling at the completion of the mold cycle will induce considerable supercooling and have homogeneous nucleation of crystallites [8] of widely varying sizes and possibly widely varying degrees of perfection. It may be seen that for such a structure, upon melting, a broad diffuse endotherm with a single peak is obtained.

Annealing at a temperature below the peak in the fusion endotherm for the unannealed specimen results in an endotherm exhibiting two peaks, separated by the anneal temperature, the relative sizes of which depend, in the first instance, upon the anneal temperature. The low temperature peak may be a result of the melting at the anneal temperature of that fraction of the crystallite distribution with a

melting point at or a few degrees in excess of the anneal temperature. On cooling, a range of crystallite sizes is formed at a temperature determined by the anneal temperature [9] and cooling rate. This crystallite size distribution is characterized by the shape and position of the low-temperature endothermic peak.

The high-temperature peak may be the melting of those crystallites formed during the initial mold cycle which did not melt during annealing. That this peak shifts to higher temperatures for higher anneal temperatures is a result of truncation of the low-temperature side of the crystallite distribution curve above the peak in the curve. Truncation of the curve below the peak will produce a curve with a different distribution, but the same peak position. For this reason the position of the high-temperature peak of the annealed material is never at a lower temperature than the single peak of the unannealed material.

Recrystallization at the anneal temperature may occur depending upon the degree of supercooling and the time available [10]. Annealing below $100°C$ for 10 min produces a secondary peak or an apparent "hump" on the high-temperature peak approximately $6C°$ above the anneal temperature. This was shown by Okamoto [11] to be due to recrystallization during annealing by scanning directly to higher temperatures from the anneal temperature. That the double peaks have their origin in the cooling from the anneal temperature [12, 13] and not recrystallization during the DSC fusion cycle [14] is shown by Fig. 2 where the relative sizes of the peaks do not change with heating rate. Further evidence that the double peaks in this material do not result from the fusion cycle is provided by the result that the material produced by the anneal cycle has a peak melting temperature below the anneal temperature [15]; whereas recrystallization at the anneal temperature could produce crystallites with a melting point higher than the anneal temperature.

The annealed sample thus may contain crystallites of three origins:

1) Those originally formed when cooled from the melt and which survive the anneal cycle.
2) Crystallites formed from the partial melt during cooling from the anneal temperature.
3) Those recrystallized at the anneal temperature.

The total effect of this restructuring is the familiar increase in crystallinity with increasing anneal temperatures.

Mechanical Testing

Since tensile testing of polymers encounters the usual problems of necking instability, leading to nonuniform strain and difficulty in
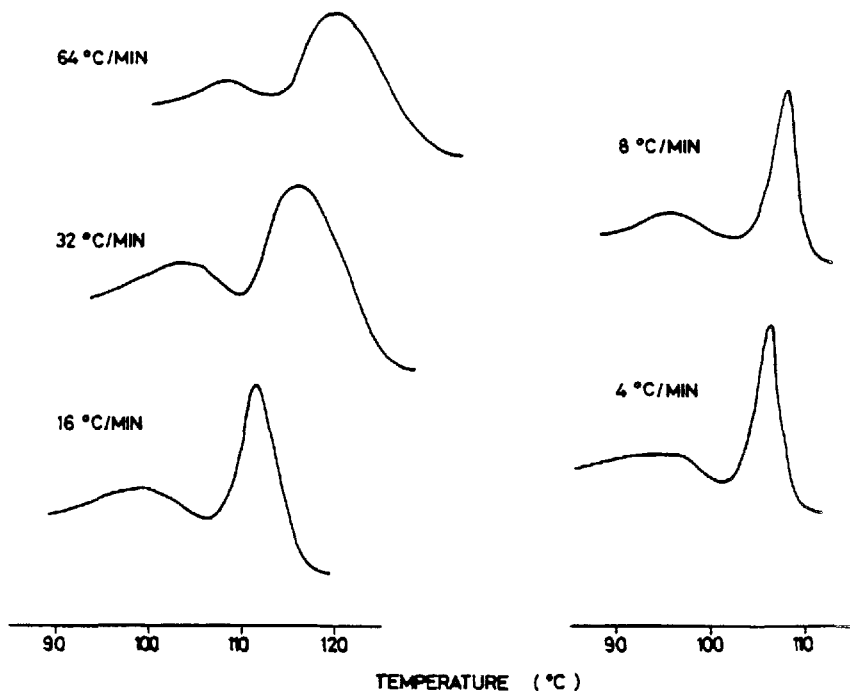
FIG. 2. Effect of increasing the DSC scan speed. No temperature correction has been made for thermal lag.

establishing true stress state, plane strain compression testing was employed to examine the yield point of polyethylene. This technique permits the determination of true stress-strain curves from simple measurements of load and displacement. The technique followed was based on that described by Williams and Ford [16]. The extrapolated yield point was determined as described by Bowden and Young by extrapolation of linear regions of the stress-strain curve above and below the yield point.

All compression tests were carried out on an Instron machine with an environmental cabinet which controls the test temperature at $25 \pm \frac{1}{4}C°$. The die faces were hardened, ground flat to within ± 0.00025 in., and polished. Parallel alignment of the dies to within 0.0005 in. over their 3 in. length was achieved by placing shims under the straining rods and die mounts. Monitoring the alignment during the course of the test was accomplished by comparing the signal from displacement transducers at either end of the dies.

This enabled nonalignment of less than 0.0005 in. to be detected, and during the course of the tests this never exceeded 0.0015 in. Machine deflection was eliminated from the results by recording load against displacement measured at the die faces by a strain gauge extensometer attached directly to the dies.

In order that the testing loads were kept below the arbitrary figure of 5000 lb, a test area of $1\frac{1}{4}$ in.^{2} was decided upon. This choice determined all other dimensions of the apparatus, which were controlled by the conflicting requirements that the specimen should be subjected accurately to plane strain conditions, that errors due to changes in the slip-line field during deformation should be minimized, and that the strain in the specimen should be determined to 1%.

For plane strain conditions to be satisfied and the area under load to remain constant, the amount of lateral spread parallel to the axis of the dies must be minimized. It was found for polymers [16] that if the width of the specimen is greater than four times the breadth of the dies, then the constraint of the material outside of the dies is sufficient to ensure plane strain.

The total load causing plastic deformation, depends not only upon the thickness of the strip and hence the strain value, but also upon the ratio of die breadth to the specimen thickness. This ratio changes continuously as the specimen is compressed, and for each value of this ratio there will be a corresponding slip line field. The result is that there are superimposed upon the basic compressive stress/compressive strain curve a series of maxima and minima, the minima occurring at those points where the ratio (die breadth/specimen thickness) passes through an integral value, and the maxima occurring in between these values. Watts and Ford [17] have shown that for values of the ratio (die breadth/specimen thickness) greater than 3 the maximum error introduced by ignoring the variation is less than 1%.

Combining these conditions leads to the use of a sample of $2\frac{1}{2}$ in. width and a die of $\frac{1}{2}$ in. breadth. The die breadth of $\frac{1}{2}$ in. gave a width/breadth ratio of 5 which ensured plane strain conditions. If the initial thickness of the specimen was 1/8 in., then the breadth/thickness ratio was always greater than 4, thus reducing the effect of this term on the yield stress to $\frac{1}{2}$% or less.

Frictional forces were virtually eliminated by the use of a molybdenum disulfide grease, which has been shown by Williams [18] to reduce the errors due to these effects to a constant factor of less than 2%.

An example of a typical load deformation curve is given (Fig. 3) showing the method of determination of the yield point. Close control of all stages of processing and annealing described earlier enabled yield stress values to be reproducible to within 2%. The variation of yield stress with anneal temperature is shown in Fig. 4 with the well-known increase in strength with anneal temperature.
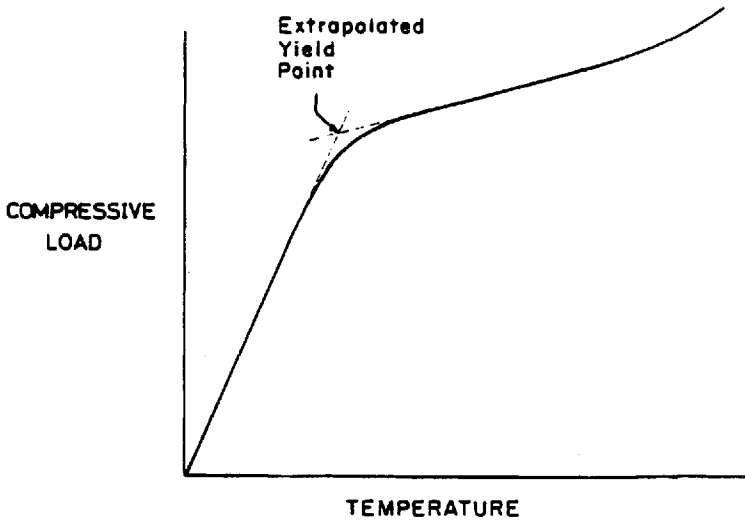
FIG. 3   A typical plane strain compression load-deformation
curve, showing the method of determination of the yield point.

Preliminary results of the variation of yield stress with strain
rate are presented in Fig. 5. To date, specimens annealed at 100 and
104°C have been tested at four strain rates with the results as shown.

DISCUSSION

The principal point of interest in these results is the increase in
yield stress with anneal temperature and the reasons for this
suggested by the proposed model. The model predicts a linear re-
lationship between yield stress and logarithm of the strain rate (Eq. 3),
and the preliminary results for this series of tests shows this (Fig. 5).
For samples with different structures (i.e., different anneal temper-
atures) the yield stress vs log strain rate graph shows curves sub-
stantially parallel but displaced vertically in relation to each other.
The gradient of the curves for a given test temperature is con-
trolled by β, and, for the two sample structures examined, β is
reasonably constant, so apparently a similar dislocation mechanism
is operating in each structure. The vertical displacement of the
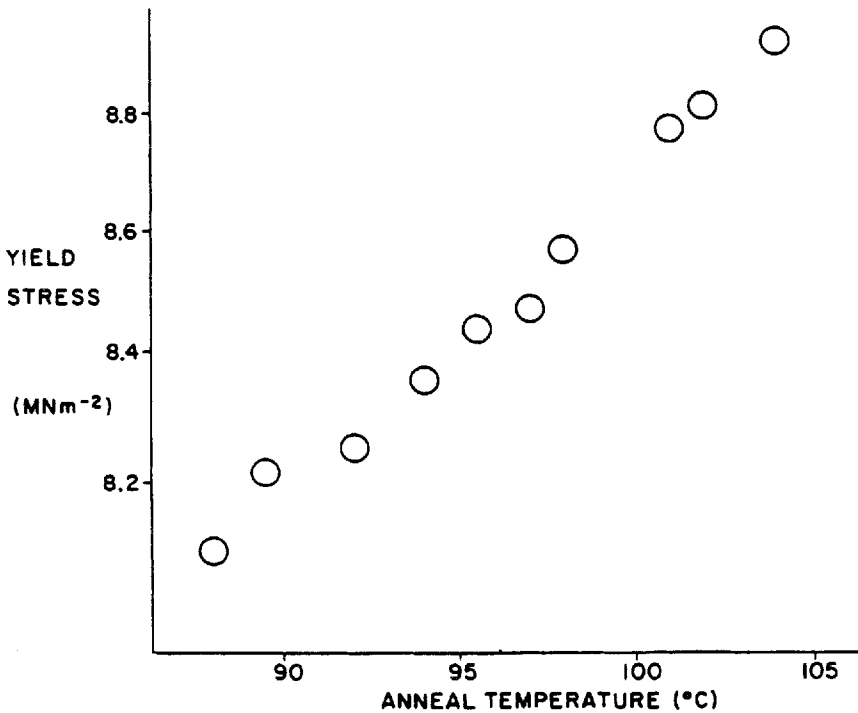curves is controlled by the last three terms on the right-hand side

FIG. 4. Variation of yield stress with anneal temperature for low-density polyethylene.

of Eq. (3). The last term contains R, a constant by definition, and verified by experiment [5]; and G_e, which changes by less than 2% for the two structures examined. Since we have to account for a change in τ_f of the order of 10%, the contribution of this term can be considered small. The term β is seen to be constant from the gradient of the curves, and hence $2\epsilon_0/\beta$ is not responsible for the change. In the remaining term the only known variable is ρ, the defect density. The results then indicate that with an increase in anneal temperature the defect density decreases. Holland [19] has observed a thousandfold increase in dislocation density after annealing of isothermally crystallized single crystals, and a decrease of dislocation density with increasing anneal temperature is not an unexpected result. The increase in crystallinity with anneal temperature also supports this conclusion.
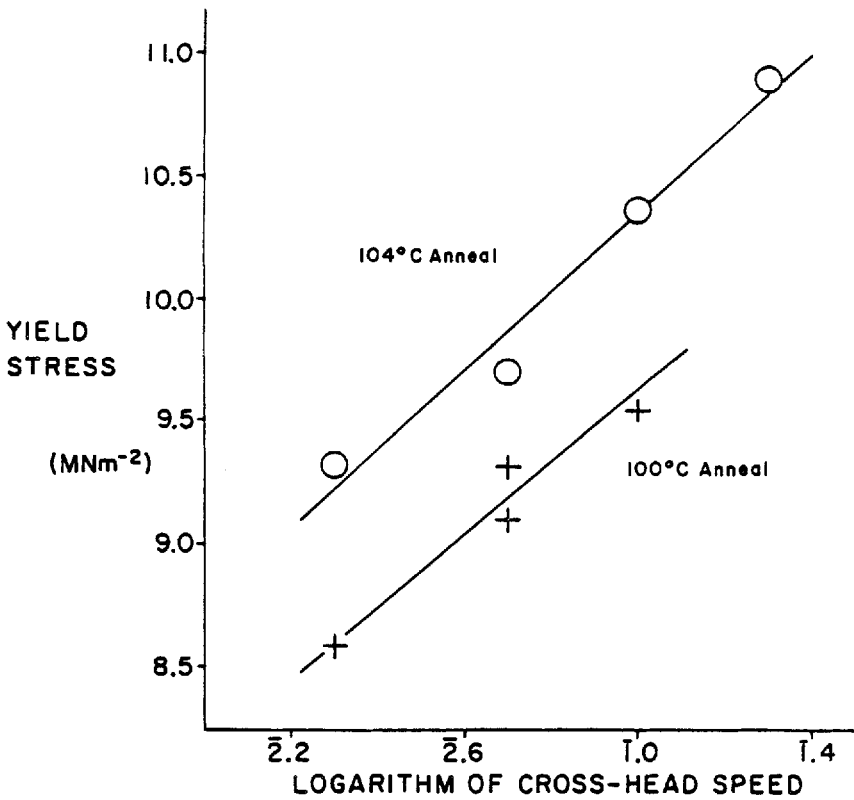
FIG. 5. Variation of yield stress with logarithm of the strain rate for two anneal temperatures.

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