A study of the effects of annealing on the mechanical stiffness and structure of ultra high modulus linear polyethylene

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Measurements have been made of the changes in Young's modulus and structure which occur when ultra high modulus linear polyethylene is subjected to different annealing treatments. The structural measurements include the determination of the linewidths of the (200), (020) and (002) X-ray reflections, and the long period obtained from small angle X-ray scattering. It has been found that there is an excellent correlation between the Young's modulus and the longitudinal crystal thickness. This correlation holds for all annealing treatments including those which involve annealing followed by rapid quenching which leads to an initial fall in modulus followed by a significant rise, as reported by previous workers.

INTRODUCTION

In a previous publication[1] longitudinal crystal thickness measurements on ultra-high modulus linear polyethylene (LPE) were reported, together with small angle scattering data and measurements of the apparent crystal modulus. It had also been found[2] that there is a good correlation between the longitudinal crystal thickness and the dynamic mechanical plateau modulus at −50°C. This correlation can be explained on a quantitative basis in terms of a model for the structure in which the aligned lamellar stacks present in oriented material of comparatively low draw ratio (~10) become increasingly linked by crystalline bridges with increasing draw ratio.

In the first instance this correlation was shown to hold for drawn and hydrostatically extruded LPE with a range of degrees of orientation produced by different draw ratios or extrusion ratios[2]. The present paper describes results for high draw ratio ultra-high modulus linear polyethylene sheets annealed at various temperatures. In view of the remarkable results which can be obtained for annealing followed by rapid quenching, in which an immediate fall in Young's modulus is followed by gradual increase over several hours, reported by Arridge, Barham and Keller[3], results are also presented for similar complex annealing procedures.

EXPERIMENTAL

Preparation of specimens

The specimens used were all in the form of highly oriented sheets, prepared from two grades of LPE, Rigidex 50 ($\bar{M}_w$ = 101 450, $\bar{M}_n$ = 6180) and H020–54P ($\bar{M}_w$ = 312 000, $\bar{M}_n$ = 33 000) (BP Chemicals International Ltd). Since the full details of the methods used to prepare the oriented sheets have been discussed in previous publications[4–6] only a summary will be given here.

Sheets of the polymers of thickness about 0.5 mm were prepared by compression moulding and quenching in cold water at room temperature. Dumbbell specimens with gauge dimensions of either 20 mm x 5 mm or 20 mm x 2 mm were cut from these isotropic sheets and drawn in air on an Instron tensile testing machine at a crosshead speed of 100 mm/min. The draw ratio λ, was measured from the separation of small ink dots marked at intervals of 1 mm on the undrawn dumbbell gauge length. *Table 1* summarises the preparation procedures for all the specimens.

After drawing, two sets of specimens were prepared by annealing at constant length. For the first set drawn specimens of H020 grade were annealed at various temperatures for 3½ h in an air oven, and allowed to cool down to ambient temperatures comparatively slowly. All measurements on these samples were made at least 24 h after the annealing procedure. For the second set, drawn specimens of R50 grade were annealed at various temperatures for 2 h in a silicone oil bath. These specimens were then quickly removed from the oil bath and immediately quenched into iced water. Measurements were made on these specimens both immediately and after the elapse of 24 h. Specific details of the annealing temperatures are given in *Table 2*. A specimen of

Table 1

Sample	Dumbbell gauge dimensions	Draw temperature (°C)	Draw ratio
Rigidex 50	20 mm x 5 mm	75	30
H020-54P	20 mm x 5 mm	95	22

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Table 2

Sample	No.	Annealing temperature
Rigidex 50	R0	–
	R1	125
	R2	130
H020-54P	H0	–
	H1	80
	H2	110
	H3	124
	H4	128
	H5	135

both grades was reserved in the as-drawn state for comparison purposes.

Mechanical properties

Dynamic mechanical measurements in the temperature range –13 to +110°C were performed on all samples of the H020–54P grade to obtain E_d, the dynamic Young's modulus in the axial direction. All measurements were performed at 20Hz. The techniques involved in the measurement of E_d on drawn films have already been reported in a previous publication[7].

The room temperature creep behaviour of the Rigidex 50 grade specimens was studied immediately after annealing and again 24 h after annealing. From the creep response, the 10 sec isochronal stress-strain curves were constructed, and the values of the creep modulus were obtained at a strain of 0.1%.

Wide angle X-ray diffraction measurements

Measurement of mean crystal thickness. Crystallite size studies were made on the samples by direct evaluation of the crystallite dimensions from the broadening observed in the wide-angle X-ray scattering. The method has been described in detail in the previous paper[1].

Briefly, measurements of the (200), (020) and (002) reflection profiles were made over an angular range of 5° (2θ) centred on the peak, using a Siemens X-ray diffractometer with step scanning facility. The scan increments were 0.02° or 0.05° (2θ) as appropriate. The observed profiles were corrected for instrumental and Kα doublet broadening by means of Stokes' method[8]. Crystal thicknesses in the three principal crystallographic directions were derived from the integral breadth of the appropriate reflections.

In accordance with the mechanical measurements made on the annealed and rapidly quenched specimens, crystal thickness measurements were made immediately after annealing and then again after 24 h.

In all cases the X-ray measurements were carried out at room temperature.

Crystal strain measurements. Measurements of the apparent longitudinal crystal modulus of the annealed specimens were undertaken in a manner identical to that described in previous publications[1,9].

The basic technique of the X-ray measurement of crystal modulus was to determine the Bragg angle of the (002) reflection as a function of applied load. A series of loads was used for each of the specimens and the lattice strains determined. Making the assumption of homogeneous stress in the specimen, a graph of lattice strain versus applied stress yields a value of an elastic modulus which we call the apparent crystal modulus.

All such measurements were made at room temperature.

Small angle X-ray scattering (SAXS)

SAXS patterns were obtained using a Kratky small angle camera with CuKα radiation monochromatised by a graphite monochromator. The scatter patterns were recorded photographically and subsequently converted to plots of relative intensity versus scattering angle using a Joyce–Loebel microdensitometer. The relative intensity was desmeared to remove the effect of slit collimation using the procedure of Chu and Tan Creti[10], and the Lorentz correction was applied to the results following the procedure derived by Hosemann and Bagchi[11]. The long spacing L, was obtained from the peak position in the plot $I(\theta)\cdot\theta^2$ versus 2θ.

RESULTS

Mechanical properties

The variation of the dynamic Young's modulus E_d determined at –13°C as a function of annealing temperature, is shown in *Figure 1* for the specimens of H020–54P, H0 to H5. The most obvious feature of these results is the strong dependence of E_d, as determined at –13°C, on the annealing temperature, T_A. Above an annealing temperature of 110°C, E_d suffers a sharp decrease from the unannealed value of ~80 GPa to a value of ~40 GPa at the highest annealing temperature.

The variation of the 10 sec isochronal creep modulus determined at room temperature for the annealed and rapidly quenched specimens is shown in *Table 3*. Close inspection of *Table 3* reveals the following. (a) Immediately after annealing and rapid quenching the creep modulus falls

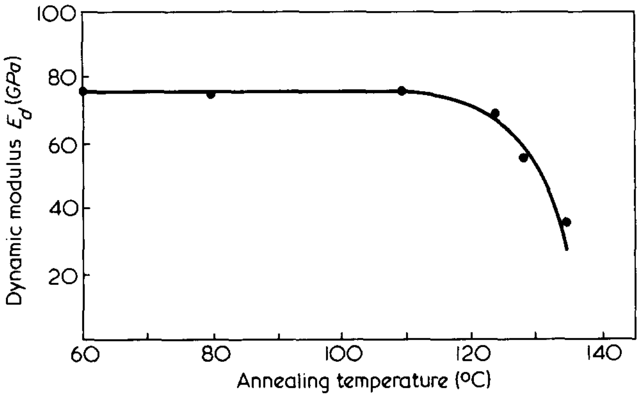

Figure 1 The dynamic modulus *E* as a function of annealing temperature T_A, determined at a temperature of –13°C, for specimens H0 to H5

Table 3

Sample	Annealing temperature T_A	*E*(0) (GPa)	*E*(24) (GPa)
R0	–	57 ± 3	–
R1	125	35 ± 2	41 ± 2
R2	130	18 ± 2	25 ± 2

E(0) Room temperature creep modulus immediately after annealing
E(24) Room temperature creep modulus 24 hours after annealing

Table 4

Sample	T_A (°C)	$\bar{L}_{200}$ (Å)	$\bar{L}_{020}$ (Å)	$\bar{L}_{002}$ (Å)	L (Å)
H0	–	116	127	439	215
H1	80	122	132	430	215
H2	110	126	137	421	215
H3	124	132	143	394	260
H4	128	141	154	384	270
H5	135	183	179	362	410

The uncertainties in the crystal thickness measurements vary from about 5% for $\bar{L}_{020}$ and $\bar{L}_{200}$ to 7% for the larger values of $\bar{L}_{002}$

Table 5

Sample	T_A (°C)	$\bar{L}_{002}$ (0) (Å)	$\bar{L}_{002}$ (24) (Å)	L (Å)
R0	–	464	–	198
R1	125	400	436	245
R2	130	350	440	295

Uncertainties in the values of $\bar{L}_{002}$ are about 7%

to a lower value, this value decreasing with increasing annealing temperature in agreement with the results reported above. (b) Subsequent measurement of the creep modulus reveals an increased value in both cases. This effect has been reported previously by Arridge *et al.*[8], and has been termed by them 'self hardening' (perhaps more properly 'self stiffening'). We note at this stage that although the present specimens also exhibit the same type of behaviour, the magnitude of the effect is very much diminished as compared with that reported previously, where the modulus was observed to recover to its initial value.

Wide angle X-ray diffraction measurements

Mean crystallite thicknesses. Mean crystallite thicknesses in the three principal crystallographic directions, ($\bar{L}_{200}$), ($\bar{L}_{020}$) and ($\bar{L}_{002}$) are shown in *Table 4* for the specimens of H020–54P grade LPE. Here we note a strong dependence of the mean crystallite thicknesses $\bar{L}_{200}$, $\bar{L}_{020}$ and $\bar{L}_{002}$ on annealing temperature. The main features of these results are that the transverse mean thicknesses increase with increasing annealing temperature and the longitudinal mean thickness decreases with increasing annealing temperature.

Table 5 shows the value of $\bar{L}_{002}$ determined for the annealed and rapidly quenched specimens, both immediately after quenching and after 24 h. It is immediately noticeable that the deduced values of $\bar{L}_{002}$ show the same trend as the values of room temperature creep modulus i.e. $\bar{L}_{002}$ decreases when the specimen is annealed but increases on subsequent storage. Also $\bar{L}_{002}$ decreases with increasing specimen annealing temperature, an observation entirely consistent with the results reported above.

Crystal strain measurements. The value of apparent crystal modulus E_c^{app}, determined from wide-angle X-ray diffraction measurements are shown in *Figure 2* in terms of their dependence on the annealing temperature T_A. Once again we note a strong dependence on annealing temperature. E_c^{app} rises from a value of approximately 170 GPa to a final value of 266 GPa for the most highly annealed specimen. These values are entirely consistent with those reported previously[1], where we found room temperature values of E_c^{app} of ~160 GPa for as drawn specimens and a value of ~240 GPa for a specimen of draw ratio 9 annealed freely at 129.5°C. No measurements of E_c^{app} were undertaken on the annealed and rapidly quenched materials due primarily to the duration of the experiment concerned.

Small angle X-ray scattering

Finally we report the effect of annealing temperature on the long period L as determined from the SAXS measurements. The values of L are shown in *Figure 3* as a function of annealing temperature for the specimens H0 to H5. An increase in long period is observed with increasing annealing temperature as previously observed by Fischer and Schmidt[12]. The data of Fischer and Schmidt are included in *Figure 3* for comparison, and the agreement between the two sets of data is good despite the fact that the two series of specimens are not identical.

The values of L determined for the specimens R0, R1 and R2 are included in *Table 5*. Once again there is a strong dependence of L on annealing temperature, in qualitative agreement with the trend shown in *Figure 3*.

DISCUSSION

Before attempting any detailed quantitative analysis, it is valuable to consider the overall features of the present results. Examination of *Figure 1* and *Table 4* shows that a fall in the dynamic Young's modulus is accompanied by a corresponding fall in the average longitudinal crystal thickness, and

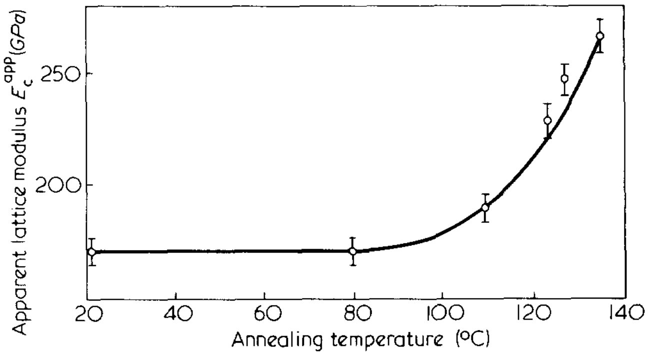

Figure 2 The apparent crystal modulus E_c^{app}, as a function of annealing temperature T_A, determined at room temperature

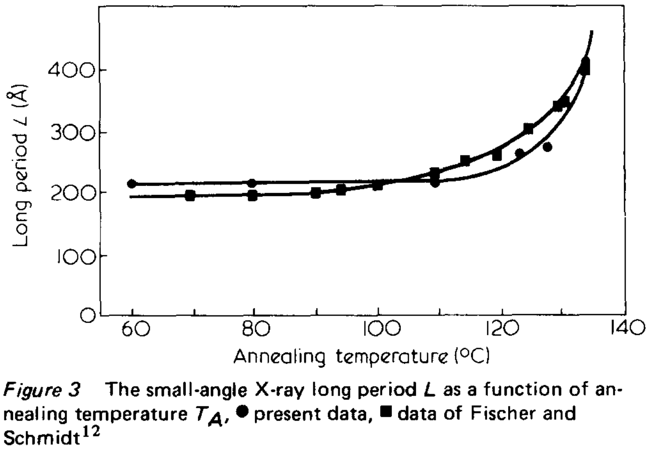

Figure 3 The small-angle X-ray long period L as a function of annealing temperature T_A, ● present data, ■ data of Fischer and Schmidt[12]

that both decrease monotonically with increasing annealing temperature. Moreover, inspection of *Tables 3* and *5* reveals that the room temperature creep modulus and average longitudinal crystal thickness fall on annealing and rapid quenching, and more remarkably, both recover to some degree in a consistent fashion on storage at room temperature. We can conclude that the correlation previously obtained for drawn and extruded LPE samples holds in a variety of annealing conditions also. Later it will be shown that the model developed previously[2] gives an adequate quantitative interpretation of the results, but for the present purpose it will suffice to observe that an increase or decrease in average longitudinal crystal thickness can be taken to imply a concomitant increase or decrease in mechanical stiffness.

We have also seen that annealing has a marked effect on the room temperature value of the apparent longitudinal crystal modulus E_c^{app}, the value of 171 GPa for the unannealed specimen increasing to 266 GPa for the most highly annealed specimen. These results are in good agreement with those presented in our previous publication[1]. There it was argued that a value of 255 ± 10 GPa represents the ultimate Young's modulus E_c of crystalline LPE and the simplest interpretation that can be placed on the room temperature value of ~160 GPa is that a considerable fraction of the material is non-crystalline and is located, from the mechanical point of view, essentially in parallel with the crystalline fraction. It was shown that, irrespective of the details of the model, the value E_c^{app}/E_c at high temperature provides a definitive upper limit for χ, the volume fraction of crystalline material. The effect of annealing is seen as producing a simple parallel lamellar texture i.e. the crystalline and non-crystalline material behave as if they are connected in series from a mechanical point of view. The present results can be interpreted very simply on the basis that with increasing annealing temperature the morphology of the specimen is converted to a simple parallel lamellar texture. The volume fraction of crystallinity of the specimen is also dependent on the annealing temperature and increases from an initial value of 0.67 to a final value which is to a large extent indeterminate from crystal strain measurements, as will be discussed below.

As indicated in the introduction, the mechanical behaviour will be discussed in terms of a model for the structure in which the lamellar stacks characteristic of low draw ratio LPE become increasingly linked as the draw ratio is increased, by molecular chain segments which traverse the intervening non-crystalline layers but remain in crystalline register, so called crystalline bridges. These crystalline bridges, assumed to be randomly dispersed, provide a degree of crystal continuity which affects the average longitudinal crystal thickness $\bar{L}_{002}$. However, the persistence of the SAXS pattern, even at the highest draw ratios indicates that the regular 200 Å structure characteristic of the lamellar stacks is still extant in the specimens.

This model also provides a simple qualitative interpretation of the dependence of average longitudinal crystal thickness and SAXS long periods on annealing temperature. As we have already observed, $\bar{L}_{002}$ decreases with increasing annealing temperature whereas L increases. We conclude that, upon annealing, the initial 200 Å lamellar structure grows at the expense of the crystalline bridge component due to loops and chain ends withdrawing into the lamellae as the lamellar thickness increases. The higher the annealing temperature, the greater the growth of the lamellar stacks until eventually the intercrystalline bridge component is removed, and a simple parallel lamellar texture of greatly increased long period (and higher crystallinity) is produced.

The results of measurements on the annealed and rapidly quenched specimens are also open to interpretation on the same basis. Annealing and rapid quenching produces growth of the initial 200 Å lamellar stacks at the expense of the crystalline bridges, again the higher the annealing temperature the greater the growth of the lamellar stacks. It appears that subsequent storage at room temperature allows some degree of recrystallization of the crystalline bridge component.

The simplest representation of the mechanical behaviour is given in terms of a Takayanagi-type model where crystalline sequences linking two or more lamellae are in parallel with both the remaining lamellar material and the amorphous material which themselves are in series[2]. The volume fraction of these crystalline sequence is given by

$$V_f = \chi p(2-p) \tag{1}$$

and the Young's modulus of the sample is

$$E = E_c \chi p(2-p) + \frac{\{(1-\chi) + \chi(1-p)^2\}^2 E_a/E_c}{(1-\chi) + \chi(1-p)^2 E_a/E_c} \tag{2}$$

In these equations p defines the probability of a crystalline sequence traversing the disordered region to link two adjacent lamellae, E_c and E_a are the moduli of the crystalline and non-crystalline (amorphous) regions respectively, χ is the volume fraction of crystallinity. Above the γ-relaxation $E_c \gg E_a$ and the second term in this equation can be neglected. In the spirit of the Takayanagi model, the α-relaxation can be considered to affect the magnitude of E_c. In the previous paper it was, however, suggested that it is more instructive to consider that the α-relaxation affects the transfer of stress between the lamellae by the crystalline bridges. This effectively reduces E_c by a factor ϕ', which is analogous to the shear lag factor which is associated with an aligned short fibre composite. The outcome of these considerations is that for high temperature equation (2) becomes

$$E = E_c \chi p(2-p)\phi' \tag{3}$$

where ϕ' is a temperature dependent shear lag factor. The previous work suggests that at −50°C (i.e. in the region above the γ-relaxation), the shear lag factor is close to unity for all samples.

In our present studies it was not convenient to make dynamic measurements at −50°C. We therefore base our comparison on −13°C dynamic modulus data, which are quite close to −50°C data and on room temperature tensile creep data which are very much in the region where the α-relaxation is affecting the behaviour appreciably. With these considerations in mind we will therefore proceed to examine the correlation between these measurements of modulus E and the quantity $\chi p(2-p)$.

It was shown by us in a previous publication that the ratio E_c^{app}/E_c forms a definitive upper limit for the volume fraction of crystallinity χ. If we equate E_c, the true value of crystal modulus with that measured for the most highly annealed specimen, we can therefore in principle determine values of χ for all the annealed specimens. However, as noted previously, there are two competing processes which can account for the observed increase in E_c^{app} with annealing temperature; increasing crystallinity and the progressive development of a simple parallel lamellar texture. Hence

Table 6

Sample	T_A (°C)	p	χ	$\chi p(2-p)$	E/E_c	σ
H0	–	0.34	0.64	0.37	0.29	0.78
H1	80	0.33	0.64	0.36	0.28	0.78
H2	110	0.32	0.71	0.39	0.28	0.73
H3	124	0.20	0.86	0.33	0.26	0.78
H4	128	0.17	0.93	0.29	0.21	0.70
H5	135	[–0.06]	[1.0]	–	0.13	–

values of χ determined from the ratio E_c^{app}/E_c could be overestimates. Certainly at the highest annealing temperature the development of the parallel lamellar texture appears to be complete and the arguments which lead to $\chi = E_c^{app}/E_c$ are invalidated so that the fact that $E_c^{app} \rightarrow E_c$ does not imply a volume fraction of crystallinity of unity.

With this further reservation in mind we can now examine the correlation between the measured moduli and the factor $\chi p(2-p)$. Values of p are obtained from $\bar{L}_{002}$ and L using the relationship

$$p = \frac{\bar{L}_{002} - L}{L_{002} + L} \tag{4}$$

Table 6 shows the values of p, χ, $\chi p(2-p)$ and E/E_c for the series of specimens H0 to H5. Also shown in *Table 6* is the ratio of E/E_c to $\chi p(2-p)$ which we have called σ. We note that this ratio is in the range 0.7–0.8 except in that case of the most highly annealed specimen H5, where the values of p, $\chi p(2-p)$ and hence σ are negative. This latter anomaly can be attributed to the fact that the measured value of the long period is greater than the estimated value of the average longitudinal crystal thickness i.e. there are now no crystalline bridges and we have a parallel lamellae type structure, as has already been discussed.

We now turn to the case of the annealed and rapidly quenched specimens. In the absence of satisfactory values of χ for these specimens, it seems most appropriate to examine the relationship between the creep modulus and the quantity $p(2-p)$ i.e. to ignore changes in crystallinity. This is shown in *Figure 4*. It can be seen that all the points, including those for the initial unannealed specimen, lie reasonably close to a straight line through the origin. It certainly appears that there is an excellent correlation between the modulus and the calculated crystal continuity, with the assumption that the changes in crystallinity are only of secondary importance. It is particularly interesting to observe that E/E_c and $p(2-p)$ fall together on annealing and rapid quenching and recover on storage.

It is extremely satisfactory to observe that both the fall in modulus on annealing and quenching and the subsequent rise after remaining at room temperature (self-stiffening effect) can be directly related to a reduction in the value of p, followed by an increase in p as some degree of recrystallization occurs. There is clearly no need to invoke remarkable changes in shear modulus as suggested by Barham and Arridge[13] in their model for the mechanical behaviour of these materials. It is important to emphasise that although both our model and the Barham and Arridge model are formally similar in that the final equations are equivalent to those for a short fibre aligned composite, our physical interpretation of the situation in ultra high modulus LPE is quite different. We consider that the changes in modulus on drawing and on annealing and subsequent self stiffening are essentially due to changes in the volume fraction of fibre phase i.e. the crystal continuity determined by the crystalline bridges. On the other hand, Barham and Arridge consider that the increase in modulus on drawing is due to the change in shape of elements which retain their identity on drawing to become needle like crystals of high aspect ratio. Furthermore they consider that during the fall in modulus on annealing and quenching and the subsequent rise on standing at room temperature these needle like crystals also preserve their identity, but that there are changes in the shear modulus of the matrix phase, which affect the shear lag factor. We do not consider that the results presented in this paper support the Barham and Arridge model.

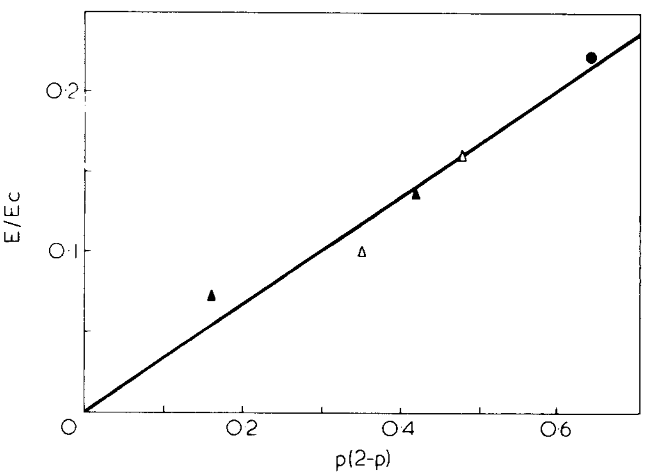

Figure 4 A comparison between the experimental values of the creep modulus (E) expressed as a fraction of the crystalline modulus, E_c, and the predictions of equation (3). ● As drawn sample, △ sample annealed at 125°C, ▲ sample annealed at 130°C

CONCLUSIONS

Annealing ultra high modulus LPE at constant length has been shown to produce systematic changes in Young's modulus, apparent longitudinal crystal modulus, mean crystal thicknesses and long period. It has been found that there is a good correlation between the Young's modulus and the degree of crystal continuity, determined from the average longitudinal crystal thickness and the long period on the basis of a statistical model for the structure proposed previously. Furthermore it appears that this model holds for all annealed specimens, including those which show the 'self-hardening' effects previously reported by Arridge, Barham and Keller.

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