Mechanical behaviour of linear low density polyethylene fibres

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The mechanical behaviour of linear low density polyethylene fibres has been investigated by means of uniaxial elongation tests and thermomechanical measurements. A mechanical model initially introduced by Grubb for HDPE fibres is proposed to account for the experimental results. This model is built on the basis of a high modulus Takayanagi-type model in which the crystalline continuity is interrupted by adjunction of a small fraction of amorphous phase in series with the mechanically active crystals. This fraction is determined by means of an original theoretical treatment of the stress–strain curves of the fibres. Correlations have been set up between this additional parameter and the mechanical properties of the fibres.

(Keywords: ethylene copolymers; fibres; Young's modulus; dynamic mechanical behaviour; mechanical model)

INTRODUCTION

During the last 10 years, improvements in copolymerization of ethylene with α-olefins have produced a new class of low density polyethylenes. The so-called linear low density polyethylenes (LLDPE) exhibit original mechanical properties as hot drawn fibres have a rather high elastic modulus close to 10 GPa, a good tensile stress at break in the range 0.5–1 GPa associated with an important residual elasticity exceeding 10%.

From the theoretical point of view, LLDPE are very useful to study the role played by the amorphous chains in the properties of drawn samples as the volume fraction of the elastomeric amorphous phase can vary over a wide range depending on the comonomer content.

In a previous paper[1], the drawability of such a material has been studied and the conditions leading to the highest ultimate draw ratio have been determined for solid state hot drawing. Thermal behaviour, molecular orientation and mechanical properties have been also investigated and reported in another paper[2]. It appeared from that work that crystallinity increases slightly during drawing while the crystalline phase orientation becomes nearly perfect after the neck propagation and the amorphous phase orientation remains poor. On the other hand, the tensile modulus increases largely with draw ratio as commonly observed for high density polyethylene (HDPE). It was suggested that the fibre stiffness is more sensitive to the number of intercrystalline tie molecules than to the chain tautness.

In this paper, we present a mechanical model based on the original elastic properties of LLDPE fibres which successfully accounts for the increase of tensile modulus with draw ratio.

MECHANICAL MODELS: GENERAL CONSIDERATIONS

The development of high modulus fibres from semicrystalline polymers has led several authors[3–8] to propose various mechanical models to account for the improvement of modulus as a result of drawing. Although the rough features of these models are based on the actual morphology of the fibres, the distribution of the crystalline and amorphous phases in the models is basically related to the degree of mechanical coupling of both phases in 'series' and 'parallel' arrangements. In fact, the analogy between the models and the actual fibres is much more mechanical than structural.

In the case of HDPE, the plastic deformation of the fibrous structure beyond necking proceeds mainly by shear displacement of microfibrils. This deformation enormously extends the interfibrillar tie molecules and enhances their contribution in the axial mechanical properties of the fibres, leading to a linear increase of the modulus with draw ratio up to values close to 100 GPa[3]. Alternatively, the formation of crystalline bridges has been proposed[4] to explain the modulus increase. This is based on the fact that the average longitudinal crystal thickness $\overline{L_{002}}$ obtained from the line broadening of the (0 0 2) reflexion is greater than the long period estimated from small-angle X-ray scattering, SAXS[8]. The melting temperature of the fibres also proved the existence of crystal thicknesses exceeding the average long period[9,10].

These two approaches have originated a mechanical model in which a part of the material (taut tie molecules or crystalline bridges) acts in 'parallel' with a 'series' arrangement of the amorphous phase and the remaining lamellar crystals. This kind of Takayanagi model is shown in *Figure 1a* where E_c and E_a are the crystalline and amorphous moduli, b is the fraction of mechanically continuous crystal and X_c is the overall crystal volume

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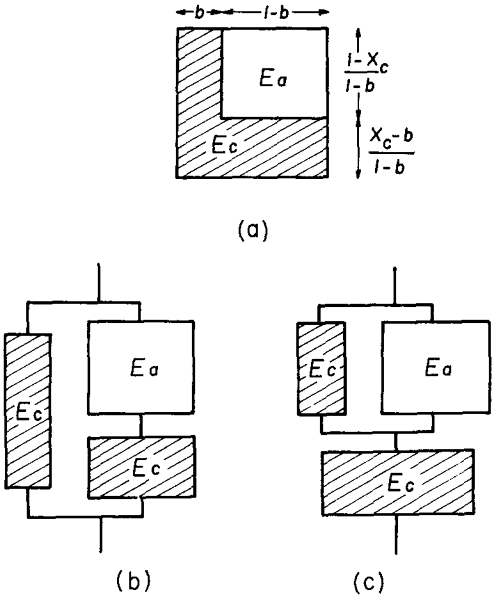

Figure 1 Mechanical models for the modulus of semicrystalline polymer fibres. (a) High modulus Takayanagi model; (b) and (c) two different ways of developing (a) in 'series–parallel' arrangements

fraction. This model can be developed in two ways (*Figure 1b* and *c*) depending on the stress distribution in the material[3,4]. Assuming that $(1-b)E_a \ll bE_c$, the first arrangement (*Figure 1b*) gives a modulus $E \simeq bE_c$ and the second one (*Figure 1c*) gives $E \simeq bE_c/(1-X_c+b)$. In both cases the increase of modulus is explained by an increase of the b fraction in the fibres. It has been previously discussed[4,5] that the choice between the two kinds of developments of the model of *Figure 1a* on the strict basis of the minimum energy criterion is not possible unless an accurate determination of the parameter b. On the other hand it has been emphasized that, on a structural basis, the model of *Figure 1b* is more appropriate than that of *Figure 1c* for drawn fibres, notably with regard to the fibrillar texture involving a molecular continuity in the drawing direction through the unfolded chains[8].

For the LLDPE studied in this work, we have previously shown that the crystalline blocks slightly thicken on drawing, but not enough for the build up of crystalline bridges[2]. Furthermore, the residual elasticity of the fibres exceeding 10%, even for the maximum achievable draw ratio $\lambda = 13$, is in major contradiction with any type of crystal continuity. So, the previous modified Takayanagi model which is successful for ultra high modulus HDPE fibres is not suitable for the much less stiff LLDPE fibres.

On the other hand, a simple 'series' model assumed on the basis of the more or less regular alternation of low elastic modulus amorphous layers and high elastic modulus crystal blocks would yield an extremely low modulus E given by the following equation[11]

$$1/E = X_c/E_c - (1-X_c)/E_a \simeq (1-X_c)/E_a \qquad (1)$$

Indeed, assuming an amorphous modulus $E_a = 0.5$ GPa[11] and considering that the volume crystallinity does not exceed $X_c = 0.6$ for the LLDPE drawn to its ultimate draw ratio[2], the 'series' model would predict a maximum value of the modulus close to 0.8 GPa which is 10 times lower than the experimental value. So, the 'series' model must be discarded for giving too large a part to the amorphous phase, from the mechanical standpoint.

We have been led to propose an alternative model which excludes crystal continuity but which does not give a predominant role to the amorphous phase. The model recently introduced by Grubb[5] seemed to fulfil very well the above conditions. Indeed, as shown in *Figure 2a*, this model assumes an interruption of the crystal continuity by narrow amorphous regions of volume fraction f with respect to the mechanically active part b. Grubb's proposal considers that these amorphous regions consist of entanglement clusters having a modulus E_1 not necessarily identical to the bulk amorphous modulus E_a. However, in the case of LLDPE, one must also consider the amorphous chains which bear the load along the fibrils as do the entanglements, namely the tie molecules which can be taut under tension. Accordingly the modulus of the additional amorphous regions should be close to E_a.

The model gives rise to four arrangements which are not very different from each other on the basis of the energy criterion[5] provided that f is small as will be shown later. Nevertheless, as suggested by Grubb, the arrangement of *Figure 2b* which is derived from *Figure 1b* is more appropriate from the structural point of view. For such an arrangement, the modulus E is given by the relation

$$E = b[(1-f)/E_c + f/E_1]^{-1} + (1-b)[(X_c-(1-f)b)/(1-b)E_c + (1-X_c-fb)/(1-b)E_a]^{-1} \qquad (2)$$

Assuming that $f \ll 1$, $E_a \ll E_c$ and $E_1 \simeq E_a$, equation (2) becomes

$$E = b[(1-f)/E_c + f/E_a]^{-1} \qquad (3)$$

This approximation is equivalent to neglecting the contribution of the right hand side of the model so that only the left hand side containing a small fraction f of amorphous phase contributes significantly to the overall modulus. The previous assumption that $f \ll 1$ leads to further simplify equation (3) into the following equation

$$E = bE_c(1 + fE_c/E_a)^{-1} \qquad (4)$$

According to this equation, the increase in tensile

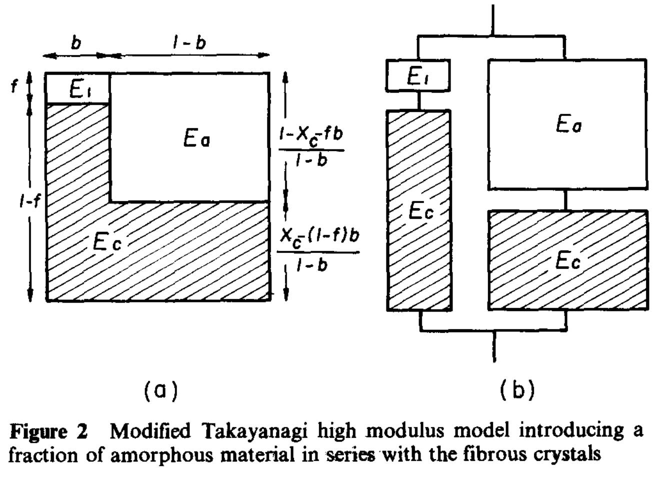

Figure 2 Modified Takayanagi high modulus model introducing a fraction of amorphous material in series with the fibrous crystals

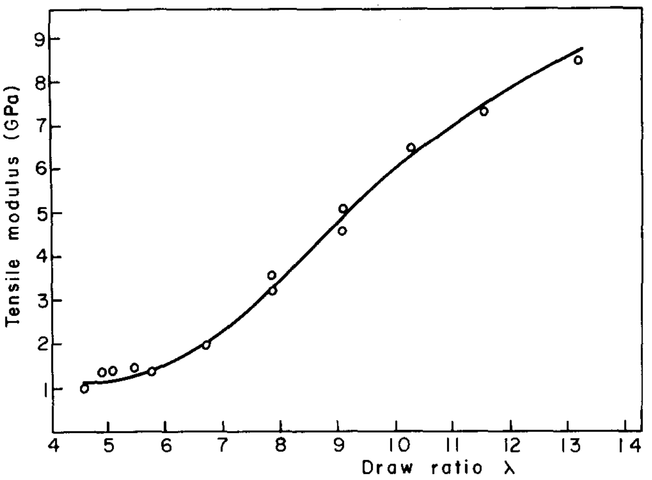

Figure 3 Tensile modulus as a function of the draw ratio λ

modulus with draw ratio can be related to a decrease of the fraction f, with a limiting value $E_{max} = bE_c$, assuming a constant value of the fraction b of the mechanically active part of the model.

In the present work we have tested the model proposed by Grubb in the case of LLDPE fibres in order to describe their specific properties. We have also developed an original means to determine quantitatively the fraction f of the mechanically amorphous regions.

EXPERIMENTAL

The LLDPE studied is an ethylene/1-butene copolymer of nominal specific gravity $\rho = 0.930$ supplied by C. d. F. Chimie. Its number and weight average molecular weights are $\bar{M}_n = 4.6 \times 10^4$ and $\bar{M}_w = 1.6 \times 10^5$. The polymer was compression moulded into sheets for 10 min at 160°C before cooling at 10°C min^{-1}.

Dumbbell specimens with gauge dimension 20 × 5 mm were cut from 0.5 mm thick sheets and drawn at 80°C in an Instron tensile testing machine at a drawing rate of 50 mm min^{-1}. Fibres having draw ratio in the range $4 < \lambda < 13$ were prepared. These fibres were subsequently tested at room temperature using a cross head speed of 1 mm min^{-1}, the sample length being 50 mm. The tensile modulus of the fibres was computed from the initial slope of the stress–strain curves.

Dynamic mechanical measurements were performed on a Toyo Baldwin DDVII-B Rheovibron in the temperature range (−135 to +45°C). The 110 Hz frequency has been selected for temperatures below −60°C in order to shift the γ transition in the temperature range accessible to our low temperature device. On the other hand the 3.5 Hz frequency has been selected for temperatures above −60°C to allow the occurrence of the α-transition before the thermal shrinkage of the samples. Indeed thermal shrinkage prohibits accurate measurements above 45°C. The fibres studied were prepared from 0.2 mm thick sheets according to the procedure used for tensile modulus measurements. The decrease in sample section with increasing draw ratio roughly compensates the increase of modulus, so that all the samples have been tested in the same ranges of strain and force.

RESULTS AND DISCUSSION

Tensile modulus

Figure 3 shows a non-linear increase of the tensile modulus E with draw ratio λ. However plotting $1/E$ against $1/\lambda^2$ in *Figure 4* gives a remarkably straight line with very little scatter within the limits of experimental errors. It is worth mentioning that this analysis of the experimental data is consistent with Grubb's interpretation of hot drawing, based on a progressive disentanglement of the molecular network with increasing draw ratio[5]. The most important implication is that the parameter f of the mechanical model should decrease as a function of $1/\lambda^2$ since f follows the tensile modulus variation according to equation (4).

Using the specific properties of the LLDPE fibres, we have attempted to establish a procedure for a direct determination of the fraction f.

Elastic behaviour of LLDPE fibres

Figure 5 represents the stress–strain curve of a fibre whose draw ratio is $\lambda \simeq 9.1$. We find in this experimental curve the typical features of a rubber stress–strain curve. These are an initial bending over towards the extensions axis characteristic of the Gaussian behaviour and a final upward curvature related to the limited extensibility of the macromolecular network. Between these two regions of opposite curvature the asymptotic limit of the Gaussian behaviour gives rise to a linear domain with a slope roughly one-third of the initial slope of the stress–strain curve.

A simple explanation of this global mechanical behaviour can be proposed in the frame work of Grubb's model. For an elastic testing limited to a macroscopic strain of 10%, the material behaviour can be primarily related to the deformation of the active part of the mechanical model, and especially to that of its most compliant amorphous component. Therefore, the experimental mechanical behaviour of the fibres should be described in terms of rubber elasticity. Consequently, a direct means to quantify the amount of mechanically active amorphous phase is afforded through the determination of its actual deformation, thanks to a fitting procedure of a rubber stress–strain curve with the

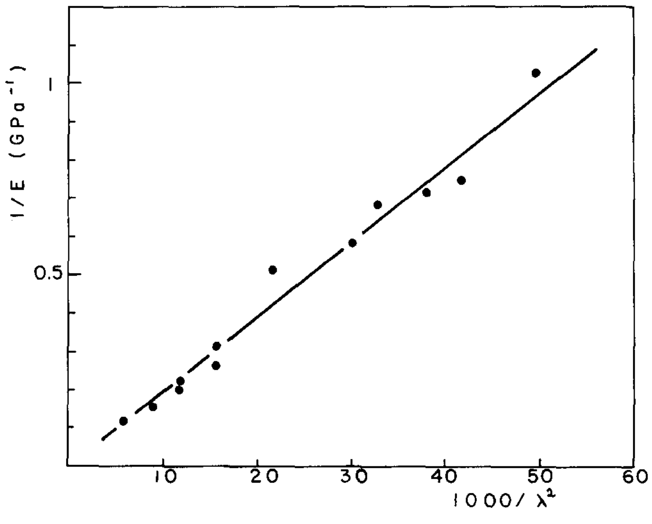

Figure 4 Compliance $1/E$ as a function of $1/\lambda^2$

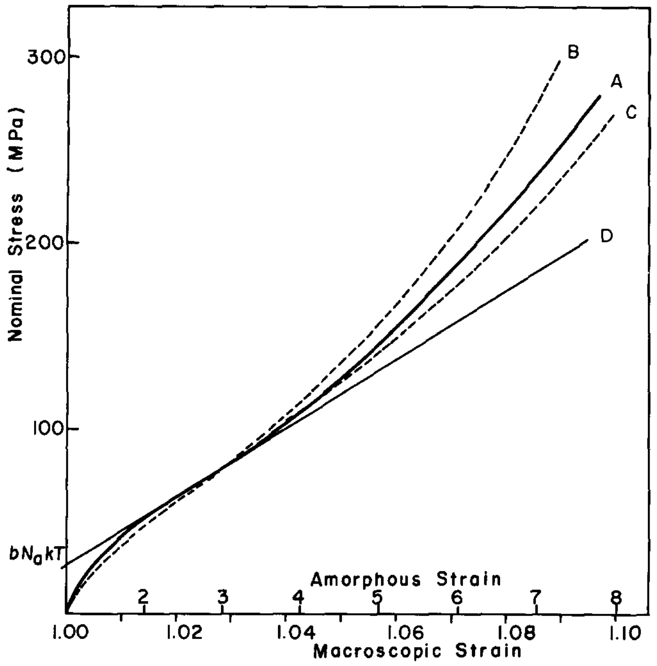

Figure 5 Stress–strain curve for a LLDPE fibre of draw ratio $\lambda \simeq 9.1$. A, experimental curve; B, theoretical curve in the inverse Langevin approximation using $n=100$; C, theoretical curve in the inverse Langevin approximation using $n=200$; D, Gaussian asymptote

experimental curve of each fibre. Indeed, the 'series' phase association that constitutes the left-hand side of the model of *Figure 2b* obeys the strain-balanced equation

$$\lambda_{\mathrm{mac}} - 1 = (\lambda_c - 1)(1 - f) + (\lambda_a - 1)f \tag{5}$$

where λ_{mac} is the macroscopic elongation and λ_c, λ_a the respective elongations of the crystalline and amorphous phases in the mechanically active part of the material. This equation can be reduced to

$$\lambda_{\mathrm{mac}} - 1 = (\lambda_a - 1)f \tag{6}$$

taking into account that $E_c \gg E_a$.

Quantitative determination of the fraction f

According to the Gaussian approximation, the stress–strain equation for a uniaxial deformation of an elastomeric network at low strains is[12]:

$$\sigma = NkT(\lambda - \lambda^{-2}) \tag{7}$$

where σ is the nominal stress, N the number of active chains per unit volume, T the absolute temperature and λ the extension ratio of the rubber network. So, in the case of LLDPE fibres, we can write:

$$\sigma = bN_akT(\lambda_a - \lambda_a^{-2}) \tag{8}$$

where N_a is the number of active chains per unit volume in the mechanically active amorphous phase and λ_a its actual elongation.

For sufficiently large λ_a values, equation (8) can be reduced to the asymptotic form

$$\sigma = bN_akT\lambda_a \tag{9}$$

This asymptotic behaviour appears on the experimental curve as the tangent at the inflexion point (*Figure 5*). The graphical extrapolation of this tangent gives bN_akT when intercepting the y-axis. Thereby the plotting of the amorphous deformation scale (λ_a) on the x-axis can be derived from $\lambda_a = \sigma/bN_akT$ (equation (9)), where σ is measured on the tangent.

Then the theoretical Gaussian curve is drawn using equation (8), giving a good fit with the first part of the experimental stress–strain curve.

The final increase of stress related to the limited extensibility of the mechanically active amorphous phase is clearly observed for draw ratio values $\lambda > 8$. In this case, the final upward curvature is well defined and the whole curve can be theoretically replotted using the inverse Langevin approximation[12]

$$\sigma = bN_akTn^{1/2}/3[L^{-1}(\lambda_a n^{-1/2}) - \lambda_a^{-3/2}L^{-1}(\lambda_a^{-1/2}n^{-1/2})] \tag{10}$$

which takes into account the limited extensibility of the network. In this equation n is the number of statistical segments between entanglements and its value is adjusted to give the best fit with the experimental curve.

For lower values of the draw ratio, plastic deformation can proceed further even at ambient temperature, prohibiting any theoretical treatment of the upper strain range of the stress–strain curves. However the assumption that the crystal is not plastically deformed during the mechanical testing of the fibres should reasonably hold true at low strains. So, as long as the asymptotic Gaussian behaviour can be determined, the asymptote can be drawn and the value of parameter f computed using equation (6).

The procedure above has been applied to a series of fibres having draw ratios in the range $5 < \lambda < 12.5$. *Figure 6* shows a plot of the fraction f as a function of $1/\lambda^2$. A fairly linear correlation is obtained within the limits of experimental accuracy. According to this result, the linear

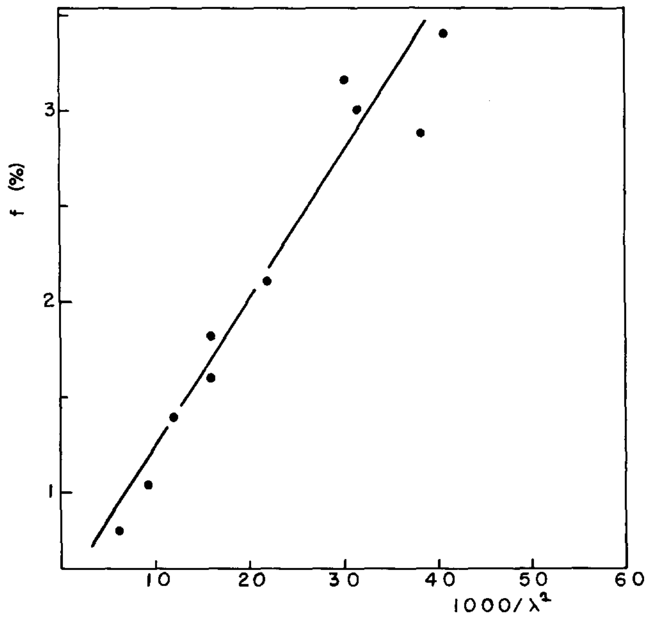

Figure 6 Volume fraction f of amorphous material in series with the mechanically active crystals *versus* $1/\lambda^2$

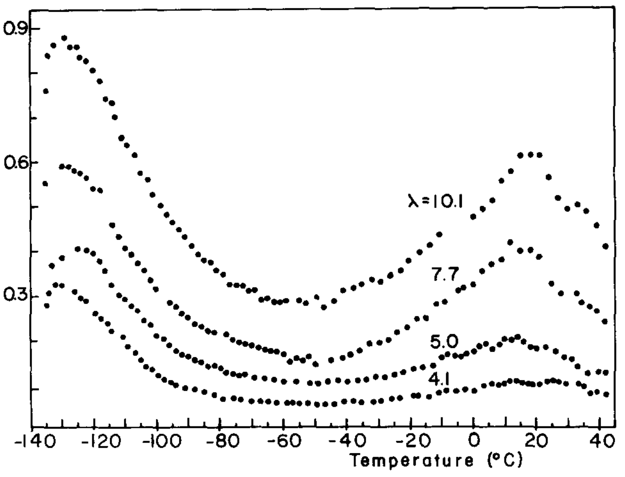

Figure 7 Variation with temperature of the loss modulus of LLDPE fibres having different draw ratios

increase of tensile modulus with $1/\lambda^2$, can be related to a reduction in the same proportion, of the amount of amorphous phase in the mechanically active part of the model.

Thermomechanical results

The variations of the loss modulus with temperature have been studied for LLDPE fibres having draw ratios between 4 and 11. *Figure 7* shows that the α and γ transitions are clearly resolved, their maxima being respectively about $+20$ and -130°C. The amplitude of both transitions increases with draw ratio, indicating that the molecular relaxations which give rise to them are sensitive to the alignment of the chains in the drawing direction. Although there has been some disagreement as to whether the polyethylene γ-relaxation could be the glass transition or not, this relaxation undoubtedly occurs in the amorphous phase[13–15]. On the other hand, the α-relaxation has been clearly identified as arising from the activation of molecular motions in the crystalline phase[14,16,17].

The magnitude of a given mechanical transition depends on the volume fraction of the phase involved[16,17]. But other factors such as orientation, dispersion and specific viscosity must be taken into account. In order to eliminate all these factors, we have studied the variation of the ratio $E''\gamma/E''\alpha$, $E''\gamma$ and $E''\alpha$ being respectively the maxima of loss modulus for γ and α transitions, as a function of the draw ratio. Since the mechanical properties of the fibres are chiefly related to the response of the mechanically active part of the material, the ratio E''_γ/E''_α should be a good parameter for following the relative changes in the volume fractions of amorphous and crystalline active phases. On the other hand, we have previously shown that the values of f are always lower than 3.5%. Therefore, the ratio $f/1-f$ is very close to f and should be proportional to $1/\lambda^2$.

Figure 8 shows a plot of the ratio E''_γ/E''_α as a function of $1/\lambda^2$ which exhibits a fair linearity considering the experimental errors.

The good agreement between these two independent results supports the validity of the model developed in this paper.

CRITICAL REMARKS

An important assumption for this model is that the fraction b of the mechanically active part remains constant with increasing draw ratio. However, in the case of the model introducing a crystalline continuity, the stiffness increase was ascribed to an increasing fraction of the continuous crystals with draw ratio[4]. In the present work the sole decrease of the fraction f can account for the stiffness increase.

There is difficulty in determining the fraction b of the mechanically active part in the model. The model described here leads to a limiting value of the elastic modulus equal to bE_c (equation (4)). This value should be in principle determined from the intercept with the ordinate axis of the linear plot of $1/E$ *versus* $1/\lambda^2$. Nevertheless this extrapolation cannot give a precise value of $1/bE_c$. Moreover the theoretical value of the crystal modulus along the chains which must be taken into account as the crystal is nearly fully oriented for $\lambda > 4$ (ref. 2) varies in the range 240–350 GPa[18].

Another possibility is to consider the value bE_a derived from the relative slopes of the linear plots giving f and $1/E$ *versus* $1/\lambda^2$ (equation (4) and *Figures 4* and *6*). This value can be estimated to 40 MPa, but E_a is not directly accessible by the experiment. E_a is generally estimated between 0.5 GPa and 1 GPa for high modulus PE fibres. However, considering that narrow crystalline lamellae inherent to the LLDPE low crystallinity[19] allow the amorphous part to contract transverse to the elongation axis[20], we can suppose that the value of E_a should be smaller than the previous value. For example, assuming a value $E_a = 0.1$ GPa leads to a quite reasonable value of $b = 0.4$. Finally, b cannot be satisfactorily determined by a mechanical approach. On the other hand, thermal analysis can afford a good means for the estimation of b as we have reported elsewhere[21].

Another parameter appears in the theoretical study of the stress–strain curves obtained at ambient temperature from fibres having draw ratio higher than 8. This parameter is the number of statistical segments n

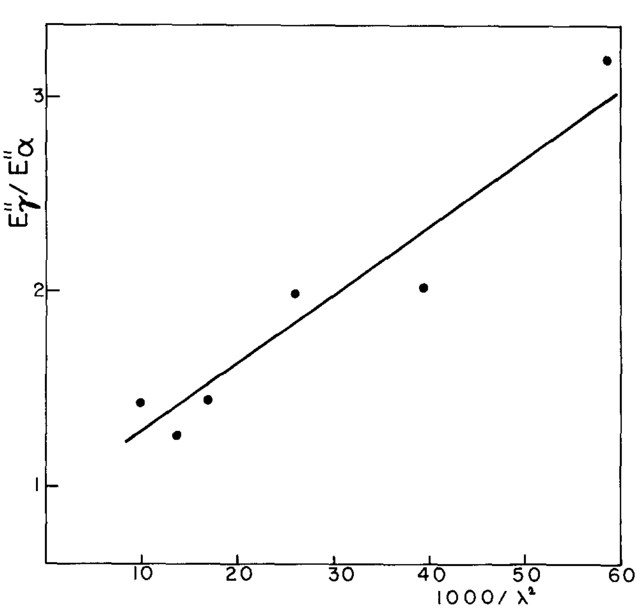

Figure 8 Ratio of the values of loss moduli at the maxima of the γ and α relaxations

introduced to give a good fitting between the experimental and theoretical curves, in the inverse Langevin approximation. The so determined values of *n* are in the range 100–300 which corresponds to a molecular weight between entanglements of several thousand grams per mole. However the theoretical treatment of the stress–strain curves postulates that the deformation is borne almost entirely by the active amorphous phase. This approximation which is reasonable for low strains is untenable for higher stress level since the crystalline phase is rather viscoelastic at the ambient temperature which corresponds to the maximum of the α-relaxation. Consequently the strain hardening of the final stage of deformation related to the limited extensibility of the network is likely to be delayed by the crystal deformation. In other words, the values of *n* determined by this method are systematically overestimated and do not contribute reliable information on the actual network.

UNDERLYING STRUCTURAL ASPECTS

We have previously mentioned that Takayanagi-type models are generally proposed to account for the mechanical behaviour of multiphase systems with little attention to the structural aspects of the problem. However, in the case of high modulus fibres, structural features have often been taken into consideration to help choose between the various ways of development of the models which depend on the stress distribution over the different phases. The well-known fibrillar texture of drawn semicrystalline polymers has notably been a basic factor for the conception of the Grubb's model[5] with a special regard to the shish-kebab structure which consists of fibrous cores with overgrowth lamellar crystals. Nevertheless, Grubb has pointed out that the main implication of a fibrous structure is a mechanical continuity without necessarily crystal continuity.

Our extension of Grubb's model offers a good alternative to the now classic explanation of the stiffness increase by development of a crystalline continuity which is untenable for low crystallinity polyethylenes. Other works[4,22,23] have already shown that the crystalline bridge model which fitted extremely well with the results from homopolymers at high draw ratios was not applicable to ethylene copolymers of comparable molecular weights and to homopolymers at low draw ratios. In fact, the absence of crystal continuity was a necessary assumption to account for the mechanical behaviour of LLDPE fibres. But this assumption appears to be an actual structural characteristic of ethylene copolymers as indicated by the comparison of the crystal thickness with the SAXS long period[1,22].

It is to be emphasized however that the decrease of the fraction *f* is liable to lead to a disapprarance of the mechanically amorphous phase and thus to the build up of crystalline bridges. Therefore, the model assuming a crystalline continuity can be considered as a limiting case of the present model from both mechanical and structural standpoints.

CONCLUSION

The Takayanagi-type model assuming a crystalline continuity to account for the high modulus of HDPE fibres is not suitable for LLDPE copolymers. The mechanical model presented in this paper is different from the previous model in the lack of crystalline continuity, which is indeed doubtful in the case of LLDPE fibres for structural and mechanical reasons. The value of the fraction of amorphous phase introduced in 'series' within the mechanically active part of the model has been determined by means of an original theoretical treatment of the fibre stress–strain curves. Its evolution with draw ratio is consistent with the variation of the elastic modulus together with the thermomechanical results.

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