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The stress-strain curve of Luflexen in tension

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This work investigated the stress-strain properties of a low density polyethylene based on novel metallocene catalysts, marketed by BASF under the trade name of *Luflexen*. It was found that the polymer exhibited rubber-like properties similar to those associated with the styrene-butadiene block copolymers. The stress-strain properties were modelled using the HT model proposed by Haward and Thackray. The model employs a dashpot to represent a viscosity in parallel with a spring defined by the theory of rubber elasticity for which non-Gaussian chain statistics were initially selected. It was shown that at extension ratios $\lambda > 2$ the model generates curves in good agreement with experimental results. A significant feature of the treatment was the ability of the model to provide an estimate of the limiting extension ratio $\lambda_{\max}$ as represented, in the model, by the parameter $n^{1/2}$.

1. Introduction

Recently a family of ultra low density polyethylenes based on novel metallocene catalysts [1] have been marketed by BASF (*Luflexen*) and by Dow (*Insite*) and a series of papers describing the properties of the latter have been published [2–5]. It was found that at densities below 0.89 g/cm^3 these Insite polymers exhibited rubber-like properties similar to those associated with the styrene-butadiene block copolymers [6, 7]. In view of the importance of this development the published treatment has been re-examined in the light of the HT model proposed by Haward and Thackray [8]. The model employs a dashpot to represent a viscosity in parallel with a spring defined by the theory of rubber elasticity for which non-Gaussian chain statistics [9] were initially selected. In this way it was possible to offer an alternative treatment for the published tensile stress-strain curves for the "Insite" copolymers to that originally used [5], which could also be applied to SBS block copolymers [10]. It was found that at extension ratios $\lambda > 2$ the new model generated curves in good agreement with experimental results. A significant feature of the treatment was its ability to provide an estimate of the limiting extension ratio $\lambda_{\max}$ as represented by the parameter $n^{1/2}$ (see below).

Following the completion of the programme, described in reference 10, BASF kindly supplied a bag of *Luflexen* 0322HX with a quoted density of 0.903 g/cm^3 and a melt index of 1.4 g/10 min. Luflexen, which is not a rubber but a tough thermoplastic with a significant yield stress, has now been the subject of a preliminary study at the Manchester Materials Science Centre the results of which are reported here. However, before presenting the actual results, a short summary will be given of the treatment used [10].

2. The application of the non-gaussian equation to rubber-like thermoplastics

Non-Gaussian chain statistics for rubber provide for a limited extension of the chain between crosslinks and leads to the following equation (Treloar [9] Equation 6.19). In this equation L^{-1} represents the inverse Langevin function.

$$\text{Nominal (or engineering) stress} = f$$
$$= \frac{NkTn^{\frac{1}{2}}}{3}\left(L^{-1}\left[\frac{\lambda}{n^{\frac{1}{2}}}\right] - \lambda^{-\frac{3}{2}}L^{-1}\left[\frac{1}{(\lambda n)^{\frac{1}{2}}}\right]\right) \quad (1)$$

Where λ is the extension ratio in tension, N the number of effective crosslinks per unit volume, and n the number of flexible units between crosslinks. Here NkT is equivalent to Treloar's rubber modulus G for which the designation C_r is used by Boyce [11] and in this paper. It is also equivalent to the strain hardening modulus for plastics G_p when this is expressed as a Gaussian equation for a solid thermoplastic.

Complications arise over the calculation of the operator L^{-1}, this being the inverse of L, where:

$$L(x) = \coth x - \frac{1}{x}$$

However, according to Cohen [12] the inverse function may be accurately approximated by a Pade equation of the form:

$$L^{-1}(x) = \frac{x(3 - x^2)}{(1 - x^2)} \quad (2)$$

As this is more easily calculated than the inverse Langevin expression and much simpler than the Taylor series reported by Treloar (9) (his Equation 6.22), it was

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checked against the inverse Langevin relation in reference 10 and found to provide a remarkably good match as claimed by Cohen [12]. Substituting Equation 2 into Equation 1 gives:

$$f = \frac{C_{\mathrm{r}}}{3}\left\{\frac{\lambda\left(3-\frac{\lambda^2}{n}\right)}{\left(1-\frac{\lambda^2}{n}\right)} - \frac{1}{\lambda^2}\frac{\left(3-\frac{1}{\lambda n}\right)}{\left(1-\frac{1}{\lambda n}\right)}\right\} \tag{3}$$

When n is large this reduces to the Gaussian equation and becomes:

$$\text{nominal stress} = f = C_{\mathrm{r}}\left(\lambda - \frac{1}{\lambda^2}\right) \tag{4}$$

The non-Gaussian Equation 3, or its simplified Gaussian form as shown in Equation 4, may be applied to experimental results for the post-yield tensile deformation of most thermoplastics for which purpose the value of the nominal stress has to be displaced upwards by a constant Y_{o}, treated as the yield stress as shown in Equation 5. This accords with the HT model and gives for the nominal stress:

$$f = \frac{Y_{\mathrm{o}}}{\lambda} + \frac{C_{\mathrm{r}}}{3}\left\{\frac{\lambda\left(3-\frac{\lambda^2}{n}\right)}{\left(1-\frac{\lambda^2}{n}\right)} - \frac{1}{\lambda^2}\frac{\left(3-\frac{1}{\lambda n}\right)}{\left(1-\frac{1}{\lambda n}\right)}\right\} \tag{5}$$

The HT model, in different forms, has been successfully applied to both crystalline and glassy polymers including polyethylene [11, 13, 14].

With rubbery materials the value of Y_{o} is generally small compared with the stresses measured at high deformations. However, with polyethylene, Y_{o} increases with crystallinity and when it becomes sufficiently large there is a fall in nominal stress with increasing strain which gives rise to necking in a conventional stress-strain test according to the Considere criterion.

3. Experimental method

A BS 2787 dumbbell test piece (Method 320C 1976) having a 40 mm parallel length and a width of 6.5 mm was stamped out of a 1.3 mm thick sheet which had been compression moulded at 115°C. The test pieces were extended using an Instron testing machine equipped with the Automated Testing System v1.02C.

Following the work of Bensason *et al.* [5], it was considered essential to measure the extension ratio (λ) in a central (25 mm) length of the test piece with an extensometer so as to eliminate distortions due to end effects. This arrangement made it impossible to use a temperature-controlled chamber so that experiments had to be carried out at ambient temperatures. However, with this procedure it was possible to measure the surface temperature changes during deformation with a contact thermometer. Experiments at an extension rate of 100 mm/min were found to give fluctuations exceeding 1°C that were reduced to 0.7°C at 50 mm/min, the testing speed used in the experiments. This corresponds to an initial strain rate of 0.013 s^{-1} and 0.002 s^{-1} at a final λ value of 6.5. Test pieces produced from a thicker 2.8 mm sheet gave higher temperature rises.

Four tests were carried out the load extension curves agreeing at all points within ±2% and these were averaged to provide the experimental nominal-stress-strain curve. As the deformation was uniform, nominal stresses could be converted to true stresses using the assumption of constant volume. All the tests were made at 23°C and a constant rate of extension of 50 mm/min. A further series of tests were also completed, at 22°C, without the extensometer, gripping the dumbbells at a displacement length of 79.5 cm so as to include the shaped ends of each dumbbell.

It was not expected that the use of a constant rate of extension, as compared with a constant true strain rate, would seriously affect the results as Bensason *et al.* [5] found that their materials were relatively insensitive to strain rate. However, methods for measuring true-stress-strain curves at a constant true strain rate have been described by G'Sell and Jonas [13] and by Hiss and Strobl [15]. The latter kindly arranged for true-stress-strain measurements to be carried out on Luflexen on the equipment designed at the University of Freiburg. For this purpose a film was moulded at 115°C and tested at 24.7°C at 0.002 s^{-1}. The results are given in Section 4.4.

4. Experimental results

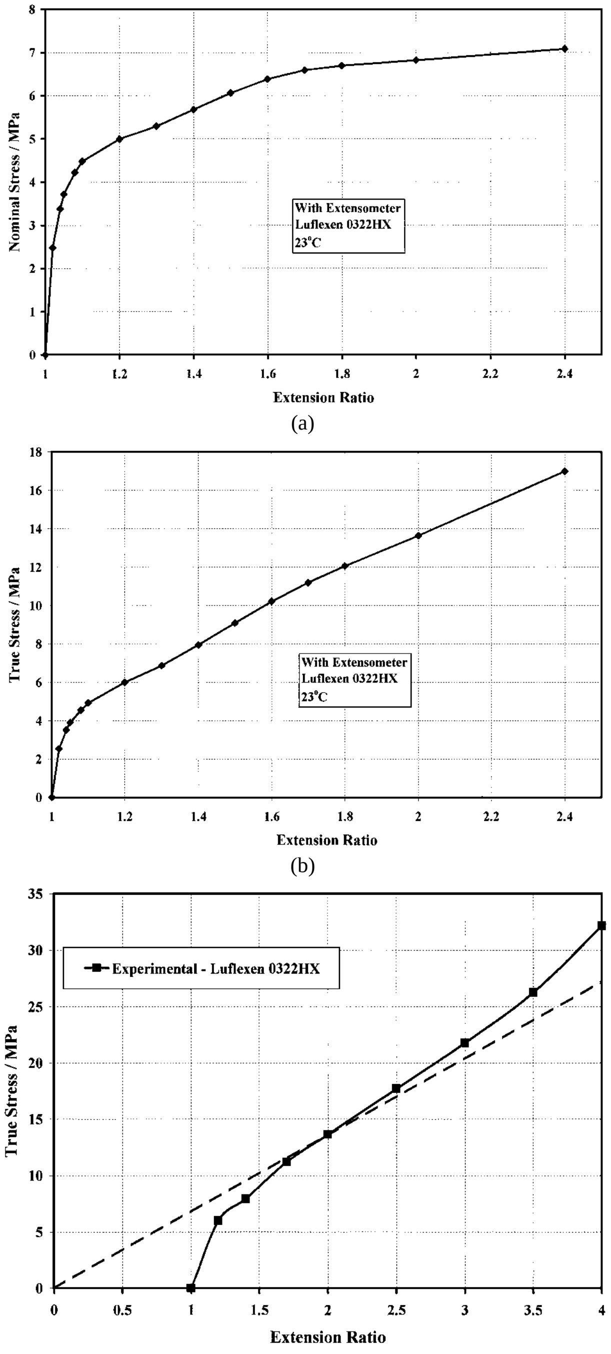
4.1. Stress-strain curve for Luflexen 0322HX at low strains

The stress-strain curve generated using the extensometer may conveniently be divided into two parts. In the first part the stress rises rather rapidly towards a yield point while the rate of strain falls by a factor of two as the extension ratio rises from 1 to 2. Beyond this point the rate of strain falls more slowly and above 2 or 2.5 the stress-strain relationship enters the large-strain region which may be represented using Equation 5. Stress-strain relations over the range of $\lambda = 1$ to 2.5 are plotted in Fig. 1a and b in which nominal and true stress are presented. It was found that uniform deformation took place not only at low strains but also over the whole deformation range as predicted by the Considere construction in Fig. 1c. This figure shows that no true tangent can be drawn from the origin to any part of the true-stress-strain curve as required by the Considere criterion for necking.

The nominal stress shown in Fig. 1a is of particular interest as it exhibits a double yield point in some ways similar to those previously reported for polyethylenes which also show large deformations in the nominal-stress range of 6–20 MPa [16, 17]. However, when the same points are plotted as a true-stress-strain relation (Fig. 1b) the second yield point is almost eliminated. Indeed the small changes in slope which can still be discerned could be due to the absence of fully isothermal conditions or to other types of experimental error. In no case is there a fall in stress as deformation proceeds. The absence of a double yield point in the true-stress-strain plot agrees with the results of G'Sell and Jonas [13] and of Hiss, Hobeika, Lynn and Strobl [18].

4.2. Results at high strains

The nominal-stress-strain curve at high strains is represented by the continuous line in Fig. 2. The filled



(a)

(b)

(c)

Figure 1 Stress-strain curves at small extensions ratios. (a) Nominal-stress-strain curve below $\lambda = 2.5$. (b) True-stress-strain curve below $\lambda = 2.5$. (c) The Considere construction for a true-stress-strain curve up to $\lambda = 5$.

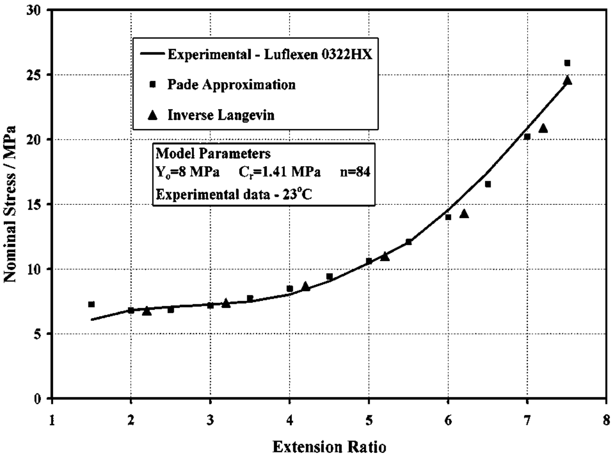


Figure 2 Nominal-stress-strain curve for Luflexen.

squares are those given by Equation 5 using the parameters shown in the figure. The data denoted *Inverse Langevin* in Fig. 2, were calculated using the same parameters, directly from Equation 1 using the inverse Langevin function plus the additional yield stress term as in Equation 5. As expected both the methods of calculation give very similar results. However, some comment is appropriate at low and high strains. At low strains the model does not attempt to follow the experimental line below $\lambda = 1.5$ as shown in Fig. 2. However, it should be noted that Bensason *et al.* [5] were able to do this with lower density (and hence lower yield stress) polymers using their more elaborate rubber-elasticity equation. With Luflexen there are fairly high frictional forces, as evidenced by the value of $Y_0 = 8$ MPa, so that the large strains are not reversible at the temperature of the test. Under these conditions the HT model [8] is felt to be more appropriate than one based solely on modified rubber elasticity theory.

The excellent agreement between calculation using the inverse Langevin function and the Pade approximation confirms previous conclusions [10, 12].

At high strains, close examination of the curve shows that the calculated points turn upwards towards their asymptote somewhat more sharply that in the experiments. Although the differences are within experimental error they have been observed in other cases and may be significant. An obvious explanation is simply the reduction in strain rate as the length of the sample increases when a constant rate of extension is used. However as the true stresses become very high under these conditions, it is always possible that the entangled system of polymer chains, which is assumed to determine n, begins to break down. It was also observed, at strains above about 6, that the test piece becomes whitened and opaque and if this was due to the formation of voids, the measured strains might also increase.

4.3. Experiments without the extensometer

As already noted, apart from the slightly higher deformations caused by minor strains outside the parallel length, deformations at low strains are similar in form whether or not the extensometer is used. At high strains however the situation is entirely different as shown in Fig. 3. Here there are small differences at intermediate strains that are ascribed to small differences in temperature and experimental error, but above nominal stresses of about 10 MPa much higher deformations are recorded in the absence of the extensometer. This is because the higher stresses successively exceed the yield stress in widened sections of the dumbbell which are then brought into the large strain process so that the parallel length, on which the calculation of strain is based, becomes too small. This should apply to most dumbbell specimens whenever the measured stress at high strain rises well above the yield stress and when strains are calculated from the parallel length of a dumbbell test piece. In such cases it is of course impossible to estimate the ultimate extensibility parameter n.

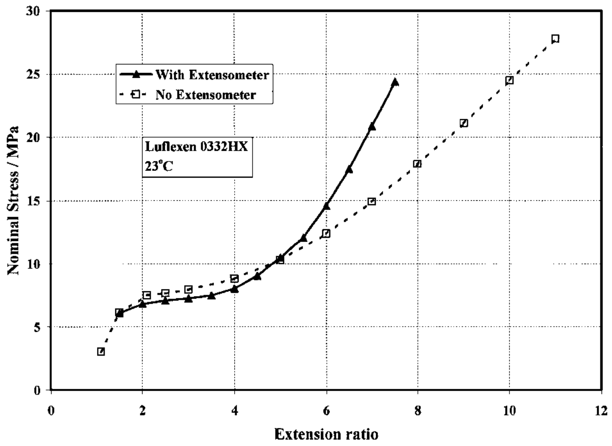
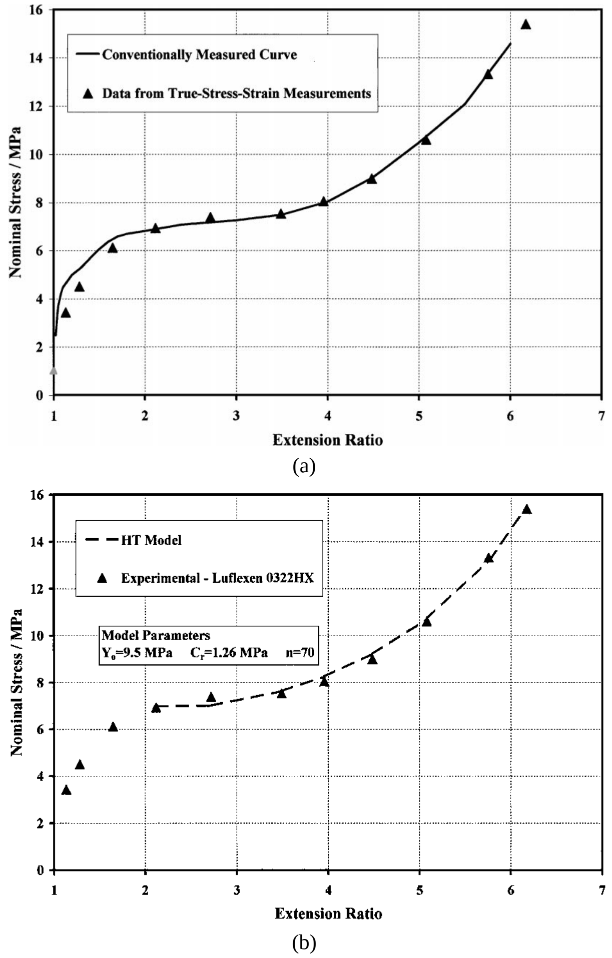


Figure 3 Comparison of the nominal-stress-strain curves with and without a central extensometer.



(a)

(b)

Figure 4 Nominal-stress constant-true-strain-rate curves measured at 24.7°C and 0.002 s^{-1}. (The original true-stress-true-strain curve was measured by Yongleng Men as described in reference [16] at the Department of Physics, University of Freiburg, Germany.) (a) Nominal-stress constant-true-strain-rate results (individual data points) and nominal-stress-strain results generated in a conventional tensile test using an extensometer (curve) as shown in Fig. 2. (b) Nominal-stress constant-true-strain-rate results plotted with a true-stress-strain curve derived using equation (5). The lower values of Cr and n are indicative of increased curvature.

4.4. True-stress-strain measurements

True-stress-strain measurements were made on the Luflexen polymer at the University of Freiburg. These results were recalculated as nominal stress, assuming constant volume, and are presented in Fig. 4a and b. Fig. 4a is a direct comparison with the results for the conventional measurements made with the extensometer. It will be seen that the agreement between the two measurements is, perhaps unexpectedly, good, taking into account the reported difference of 1.7°C in temperature (though this may have been reduced by some self-heating in the conventional test) and inevitable differences in moulding conditions. However, in spite of the lower extension reached in the true-stress-strain measurements, upon which the accuracy of n depends, the greater curvature indicated by the lower value of n may be significant since the fall in strain rate at high strains, characteristic of the conventional test, is likely to flatten the measured curve and lead to the observed difference (Fig. 4b).

5. Conclusions

Luflexen 0322HX, in line with its higher quoted density has a higher yield stress than the ultra-low-density polyethylenes described by Bensason *et al*. [5]. In conventional tensile tests it shows a double yield point which is however, hardly visible in a true-stress plot. It does not meet the Considere condition for necking and does not neck. When deformation is measured using an extensometer in a normal tensile test it is therefore possible to recalculate the measured nominal stress as a true stress measured at a decreasing strain rate. The results are readily modelled using the non-Gaussian equation (5). The same may be said of a measured true-stress-strain curve which, when plotted in terms of nominal stress agrees well with results measured conventionally.

Conventional measurements based on machine displacement with a dumbbell test piece are not suitable for measuring the limits of extensibility ($n^{\frac{1}{2}}$).

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