ELSEVIER

Polymer 40 (1999) 5821–5832

polymer

The application of non-Gaussian chain statistics to ultralow density polyethylenes and other thermoplastic elastomers

R.N. Haward*

Deptartment of Chemistry, UMIST, Manchester M601 QD, UK

Received 10 November 1998; accepted 28 January 1999

Abstract

A conventional rubber elasticity equation based on the inverse Langevin function, combined with a yield stress (Y_0) has been used for the purpose of studying published tensile stress–strain curves for thermoplastic elastomers. In order to simplify the calculation a Pade approximation has been employed [Cohen A. Rheol. Acta. 1991;30:270] for the inverse Langevin function which leads to the following equation, relating f, the nominal or engineering stress, to the extension ratio λ:

$$f = Y_0/\lambda \ + \ (Cr/3)[\lambda(3 - \lambda^2/n)/(1 - \lambda^2/n) - (1/\lambda^2)(3 - 1/\lambda n)/(1 - 1/\lambda n)].$$

When suitable values of the parameters are selected the equation may be used to model nominal stress–strain curves for the new ultralow density polyethylenes, ethylene vinyl acetate copolymers and SBS block copolymers. The parameters Cr and n selected in this way represent identifiable physical entities; Cr the initial modulus and $n^{1/2}$ the limit of extensibility. However Cr does not increase with temperature as with a conventional rubber, but declines as the temperature is raised. With the polyethylenes this may be related to the gradual melting of the crystals which are believed to act as cross links [Bensason S, Stepanov EV, Chum S, Hiltner A, Baer E. Macromols 1997;30:2436]. However, with an SBS block copolymer the reason for the fall in Cr and the rise in n are not clear. Generally, for instance when the temperature is reduced and the materials become stiff, Cr will increase and n decrease. However when it is plotted against crystallinity with the ultralow density polyethylenes, n does not follow Cr but shows a minimum at a crystallinity of 30% after which it appears to increase. With polyethylenes n is more sensitive to molecular weight than Cr and gives a linear Flory plot for $n^{1/2}$ against $1/T$ at 0°C. At 25°C the values of n obtained are very high and when the molecular weight falls to 32 000 and the stress–strain curve is found to follow a Gaussian equation. This supports the mathematical requirement that the equation reduces to a Gaussian form when n is very large. The same result can be predicted from a series approximation suggested by Treloar. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Stress–strain curves; Thermoplastic elastomers; Non-Gaussian

1. Introduction

Recent developments in the interpretation of mechanical behaviour in thermoplastics have increasingly employed concepts related to the conformation of the polymer chain [1–5]. In applying this principle to solid plastics it is common to employ the hypothesis of Haward and Thackray [4] that elastic and viscous forces may be modelled in parallel. This is especially true of the glassy polymers where Boyce and co-workers [5,6] have provided a consistent account of large strain properties in terms of entropic (chain straightening) and viscous (interchain friction) properties. For this purpose they used non-Gaussian chain statistics derived from an equation based on an inverse Langevin function described by Treloar in ‘‘The Physics of Rubber Elasticity’’ [7]. Their treatment makes it possible to represent not only deformations measured in tension, but also those resulting from the application of other types of stress such as compression and shear.

Obviously the employment of rubber elasticity theory outside the specific circumstances for which it was developed raises serious questions. For example, the classical theory of rubber elasticity is predicated by the existence of long polymer chains where bond rotation occurs freely without significant energy barriers or frictional interaction between the moving chains. A further requirement is that the polymer chains are linked by covalent bonds unaffected by changes in temperature in the range of interest. Calculations based on the configurational entropy of the chains then generate equations, which describe the well-known characteristics of reversible rubber elasticity including the proportionality of stress to absolute temperature.

At this point problems arise when equations appropriate

---

* Current address: 1A Gaddum Rd, Bowdon, Cheshire WA14 3PD, UK. Tel.: + 44-0161-941-6018.

0032-3861/99/$ - see front matter © 1999 Elsevier Science Ltd. All rights reserved.

PII: S0032-3861(99)00124-X

to conventional rubbers are applied to thermoplastics or thermoplastic rubbers where for example the measured stresses during deformation decline as the temperature is increased and where the transmission of forces between polymer molecules occurs through ‘‘entanglements’’, viscous interaction or through isolation in a second phase. Nevertheless it is reasonable to assume that the variations in entropy which accompany changes in the configuration of the polymer chain will be controlled by factors similar to those in a rubber. Models for the process may therefore be taken from one of the several models, which have been used in the theory of rubber elasticity.

Interest in this field has recently grown following the discovery of new catalysts for ethylene polymerisation capable of providing ultra low density ethylene copolymers with a more regular structure than have hitherto been available [8]. These have similarities with the thermoplastic rubbers based on block copolymers of styrene with isoprene or butadiene which have already been known for some time [9]. Recently an article of particular importance was published by Bensason et al. [10], who reported tensile experiments with rubber-like ultralow density polyethylenes, which could be accurately modelled by a rather complex rubber elasticity equation employing the additional concept of slip links [11,12] (see Appendix B).

The present work aims to show that these results together with those from ethylene vinyl acetate copolymers and the styrene–diene block copolymers may be represented by a model for large elastic deformations in tension which employs the non-Gaussian inverse Langevin relation. A further objective is to emphasize the importance of the long neglected limit in the extensibility of polymeric materials. Finally the possible implications of the conclusions reached will be discussed in relation to the introduction of entropy based contributions to theories for the deformation of crystalline thermoplastics.

2. The application of the non-Gaussian equation to thermoplastic rubbers

Non-Gaussian chain statistics for rubber provide for a limited extension of the chain between cross links and leads to the following equation ([7] Eq. 6.19). In this equation L^{-1} represents the inverse Langevin function (see Appendix A).

$$\text{Nominal (or engineering) stress} = f$$

$$= (NkTn^{1/2})/3(L^{-1}(\lambda/n^{1/2}) - \lambda^{-3/2}L^{-1}(1/(\lambda n)^{1/2})), \qquad (1)$$

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 cross links. Here NkT is equivalent to Treloar's rubber modulus G for which the designation Cr is used by Boyce in Ref. [6] and subsequently followed in this article. 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 [13].

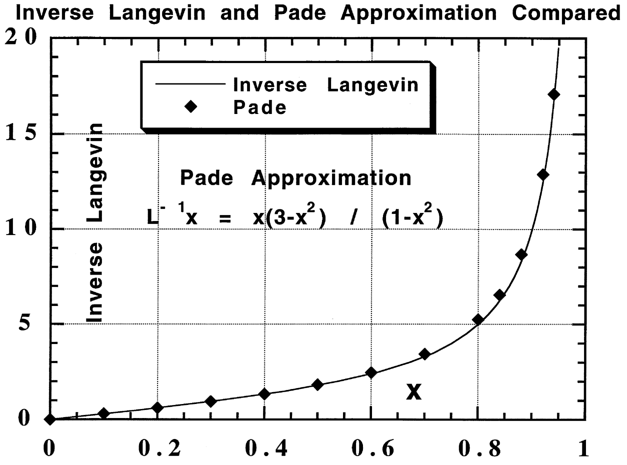

Fig. 1. The results of Cohen [14], using the Pade approximation, are recalculated and confirmed in this figure.

Complications arise over the calculation of the operator L^{-1}, where $L(x) = (\coth x - 1/x)$ and L^{-1} refers to the inverse function. However, according to Cohen [14] the inverse function may be accurately approximated by a Pade equation, viz.

$$L^{-1}x = x(3 - x^2)/(1 - x^2). \qquad (2)$$

As this is more easily calculated than the inverse Langevin expression and much simpler than the Taylor series reported by Treloar (Eq. (B.1) see Appendix B), it was checked against the Langevin relation as shown in Fig. 1. The result is the same as that published by Cohen. The Pade expression clearly gives a very good approximation and this will be used here. In another study to be published later both Eq. (1) and the Pade approximation have been applied directly to the same experimental results and good agreement has been obtained. When Eq. (2) is substituted in Eq. (1) we obtain

$$f = (Cr/3)[(\lambda(3 - \lambda^2/n)/(1 - \lambda^2/n)$$
$$- (1/\lambda^2)(3 - 1/\lambda n)/(1 - 1/\lambda n)]. \qquad (3)$$

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

$$\text{nominal stress} = f = Cr(\lambda - 1/\lambda^2). \qquad (4)$$

In applying the non-Gaussian equation to the experimental results with the thermoplastic elastomers, account has to be taken of the inability of these two constant equations to describe the initial stage of the deformation process as with the more complex equation used by Bensason et al. [10] so that it has to be displaced upwards by a further disposable constant Y_0 treated as yield stress as shown in

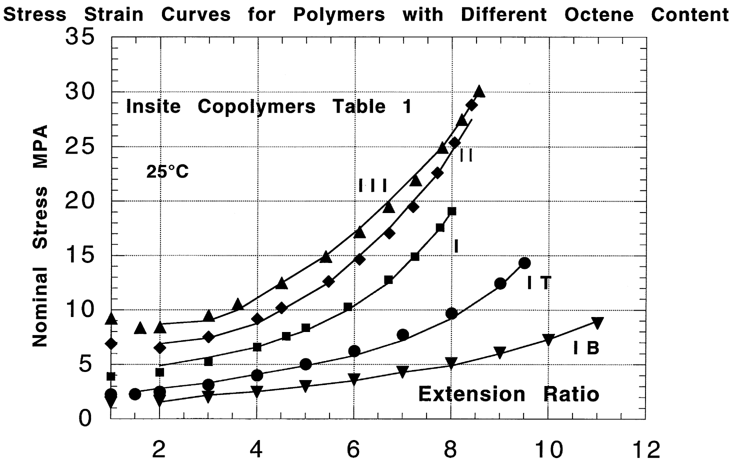

Fig. 2. The continuous lines are reproduced from the work of Bensason et al. [21,22] and the points calculated from Eq. (5) using the parameters given in Table 1.

Eq. (5).

$$f = Y_0/\lambda \; + \; (Cr/3)[\lambda(3 - \lambda^2/n)/(1 - \lambda^2/n) - (1/\lambda^2)(3 - 1/\lambda n)/(1 - 1/\lambda n)]. \qquad (5)$$

With rubbery materials the value of Y_0 is generally small compared with the stresses measured at high deformations. However with polyethylene Y_0 increases with crystallinity and when it becomes sufficiently large, as with conventional polyethylenes, there is a fall in nominal stress with increasing strain which gives rise to necking in accordance with the Considere condition.

Finally, it should be noted the when expressed in terms of true stress (σ_{true}) the Gaussian Eq. (4) becomes

$$\sigma_{\text{true}} = Cr(\lambda^2 - 1/\lambda), \qquad (6)$$

to which the yield stress may be added when appropriate [13].

In reproducing points from published curves the figures are first enlarged and then lines are drawn connecting up x and y ticks, respectively. Coordinates are then obtained by measuring the displacements within the small rectangles drawn on the graph.

3. Different types of measurement used for stress–strain curves

Several different methods of measuring tensile stress–strain curves have been reported in the literature. Those used in the results quoted here are summarised as follows.

(A) The simplest method is the nominal (or engineering) stress–strain curve where the test piece is extended at a constant rate and the force measured in a conventional tensometer is related to the original length and cross section. In the absence of an appreciable yield stress elastomers and plastics generally will extend uniformly without necking. This method, as practised in Refs. [21,22] raises certain problems. In the first place, a very high initial strain rate ($10\ \text{min}^{-1}$) was used so that the isothermal conditions may not have to been maintained, particularly with the higher crystalline materials. This uncertainty inevitably raises doubts about the variation on n with crystallinity as shown in Fig. 3, where a dotted line has been drawn. There might also have been some problems with the uniformity of the deformation in the test piece which could lead to somewhat higher measured value for Cr. These deficiencies were eliminated in the work described in Ref. [10]. Measurements by method A are all that is available for the styrene block copolymers.

(B) Method A is improved by the use of benchmarks to record the deformation of a limited length, generally at the centre of the test piece, to eliminate errors due to end effects. A good way of doing this is to deposit a rectangular pattern on the test piece by the evaporation of a deposit through a grid [10,15] and following strains through the deformation of the grid. This gives a true nominal stress–strain curve

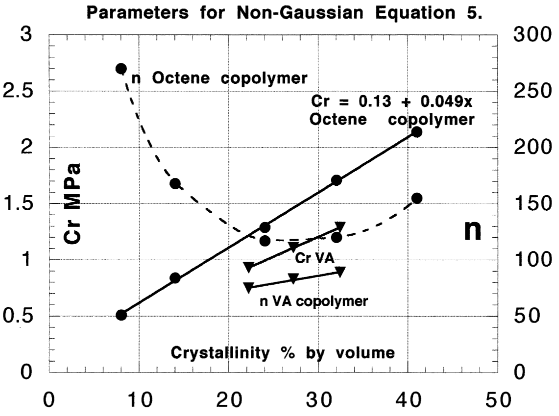

Fig. 3. The effect of crystallinity on the non-Gaussian deformation parameters. Crystallinity here is measured by volume gms or ccm of crystal per 100 ccm (crystal density 1.00). With vinyl acetate copolymers wt.% values given by DSC measurement have been converted to a volume by introducing a small correction based on the density values for polyethylene.

Table 1
Specification for octene copolymers [22]

Designation	Comonomer content (mol%)	Density (g/cm^3)	Melt index (g/10 min)	Y_o (Eq. (5)) (MPa)	*Cr* (MPa)	*n*
1B	14.6	0.865	0.5	1.50	0.51	270
IT	11.8	0.874	0.5	1.7	0.84	168
I	8.5	0.887	1.0	3.9	1.29	117
II	5.3	0.901	1.0	6.9	1.71	120
III	3.3	0.913	1.0	9.2	2.14	155

measured at a constant rate of extension. It is quite satisfactory for rubbers where the stress is relatively insensitive to the rate of strain which, of course falls slowly during the test. Under these conditions nominal stresses may be converted to true stresses by assuming constant volume and multiplying by λ.

(C) The best procedure, particularly for materials which do not show uniform deformation, is the measurement of true stress–strain curves at constant true strain rate. This method generally uses an hourglass (waisted) test piece and has been described in detail by G'Sell and Jonas [16,17], Hope et al. [18] and Hiss and Strobl [19].

3.1. The application of the non-Gaussian equation to experimental results

In this section published tensile stress–strain curves are evaluated for ethylene olefin copolymers, ethylene vinyl acetate copolymer and for styrene–diene block copolymers. It will be followed by discussion wherein the significance of the results will be considered.

3.2. Ultra low density ethylene–octene copolymers

3.2.1. The effect of octene content

Following the discovery of new types of polymerisation catalysts a series of ethylene–octene copolymers have been marketed by the Dow Chemical Co. under the trade name ''Insite''. These are all polymers with low densities and low levels of crystallinity. They have low or zero yield stress and may be regarded as thermoplastic rubbers analogous to those made from styrene and butadiene. Their introduction further increases the wide range of ethylene polymers already available and for this reason Bensason et al. [20] have reclassified the whole range of polyethylenes on a density and crystallinity basis into four types, viz. I –IV. Materials classed as Type I have densities below 0.89 and Type II extend from 0.89 to 0.905. In terms of the previously available materials both may be regarded as ultra low-density copolymers. They form an important part of the present study.

For these polymers their chemical composition is defined by the proportion of the comonomer. Details of this and of other Type I and II materials which are the first polymers to be studied here are given by Bensason et al. [21,22] and are reproduced in Table 1. Type A stress–strain curves for these polymers were also measured in an Instron machine at ambient temperatures and these are plotted as lines in Fig. 2 where they are accompanied by points calculated using the non-Gaussian Eq. (5). This demonstrates the applicability of the equation and provides values of the parameters *Cr* and *n* which are plotted in Fig. 3, together with some results from ethylene–vinyl–acetate copolymers which will be presented later. The continuous rise in the modulus *Cr* corresponds with an increase in cross linking with increasing crystallinity but the rise in *n* at high crystallinities seems anomalous and needs confirmation, as already explained. As already noted high values of *n* are associated with Gaussian stress–strain plots.

A specification of these polymers, together with the parameters for Eq. (5) are listed in Table 1.

3.2.2. The effect of temperature

In their later work Bensason et al. [10] have made a systematic study of a Type I polyethylene designated as CGCT 87. Measurements on nominal stress–strain curves were made using the improved method B at a series of controlled temperatures. They demonstrated that their results were very well modelled by the equation given in Appendix B. In this section we continue to investigate the capability of Eq. (5) to represent the same results over the range of large deformations where $\lambda > 1.5–2.0$. The resulting graphs are given in Fig. 4 and listed in Table 2. Eq. (5) is clearly able to represent the curves showing the effect of temperature in Ref. [10]. The question of the possible value of a simple and apparently more primitive model, when a more comprehensive treatment has already been published, will be included in Section 4.

From the curves in Fig. 4 values of *Cr* and *n* may be derived and these are plotted against temperature in Fig. 5(a). It is clear that at the higher temperatures the value of *n* increases with the consequence that a longer linear section is observable in the nominal stress–strain curve above $\lambda = 3.5$. This again indicates an approach to Gaussian behaviour.

3.2.3. The influence of molecular weight

In their article Bensason et al. [10] also present results for polymers of five different molecular weights viz., 20 000 (20), 26, 32, 37 and 57 K, measured over a range of temperatures. The results for three of the five curves measured at 0°C are given in Fig. 6(a) together with the calculated points and the associated parameters plotted in

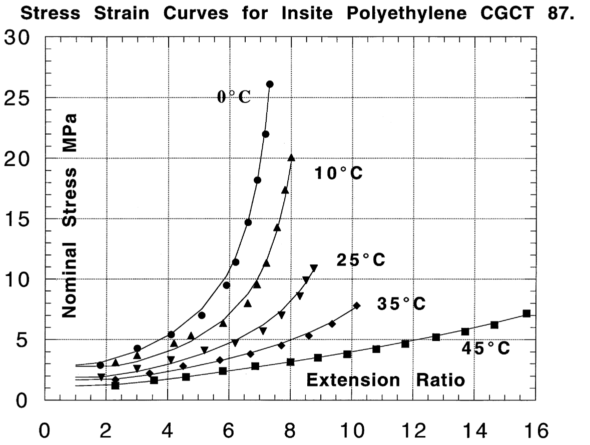

Fig. 4. Curves reproduced from Bensason [10] and points calculated from Eq. (5) using the parameters shown in Table 2. Polymer specification Comonomer 12.3%, Melt Index 0.8 g/10 min.), Crystallinity 12%, Density 0.873 g/cm^3.

Fig. 5(b). It will be seen that the changes in molecular weight have a large effect on n but only a small effect on Cr. Indeed because of the difficulty of separating the five curves at low strains, small differences between them are not significant. However direct examination of the enlarged copies supports the conclusion that there is indeed a small increase in slope in the critical range from $\lambda = 2.5$–4 with higher molecular weights. This is unexpected as Bensason et al. report a constant slip-link modulus and a falling cross link modulus under the same conditions. The curves for 20 and 57 K are repeated in Fig. 6(b) as Gaussian plots. It will be seen that the lower molecular weight polymer with a higher value of n gives a longer linear section and a value of the slopes closer to the result from Eq. 5. When n is low it is clearly possible for an apparently linear Gaussian plot to provide a modulus well above Cr because the rise in stress due to limited extensibility is included in the Gaussian line (see Fig. 14 and Section 4).

Measurements on 57, 37, and 32 K at 25°C are shown in Fig. 7. Both the two higher molecular weight polymers are fitted by the non-Gaussian equation but at 37 K the value of n was very high. With the 32 K polymer however there is no indication of a limit of extensibility and the stress–strain curve exhibits gaussian behaviour. Bensason et al. showed that at lower molecular weights and higher temperatures the curves may turn downwards and ascribe the decline in stress to the breakdown of the underlying network.

Table 2
Deformation parameters for CGCT at different temperatures (Bensason [10])

Temp (°C)	Y_0 (MPa)	Cr (MPa)	n
0	2.9	0.96	66.5
10	2.8	0.72	82
25	1.9	0.57	122
35	1.7	0.465	218
45	1.2	0.36	950

3.3. Vinyl acetate copolymers

Vinyl acetate can be copolymerised with ethylene to give EVA copolymers which, with the relatively high proportions of vinyl acetate shown in Table 3, fall into the crytallinity range associated with the ultra low density polyethylenes described earlier.

True stress–strain curves for these materials, measured by method C, have been published by Hiss and Strobl [19], in the form of true stress against Hencky strain (ln λ). These have been transformed to show the dependence of nominal stress against λ. As true stress is very much larger than the nominal stress at high strains the y-axis for nominal stress covers a smaller range of stress which has the effect of widening the visible difference between stresses for the different materials at low strains. This is not entirely associated with any improvement in the accuracy of reproduced graphs at low strains, which is limited by the small measurable distances in the published results. This particularly affects the postulated yield stress. Nevertheless the curves are well fitted by Eq. (5) (Fig. 8) so that the values of the parameters Y_0, Cr and n define the curve quite well. For example, as with the octene copolymers, Cr increases with crystallinity and, more surprisingly, n also increases over the same 30% range again as with the octene copolymers. That the results do not coincide completely is not surprising as both copolymers contain appreciable quantities of the respective comonomers (Tables 1 and 3), so that differences may be expected other than those simply related to the effect of comonomer on crystallinity.

3.4. Styrene–diene triblock copolymers

From the previous results it will be seen that the ultra low density polyethylenes and the vinyl acetate copolymers are rubber like materials whose initial modulus depends on the proportion of the crystalline phase. This, as already pointed out by Bensason et al. [10], provides multifunctional junctions acting as physical cross links in a manner analogous to other thermoplastic elastomers. It therefore seemed appropriate to apply the treatment described earlier to examples of the styrene–diene triblock polymers which have now established themselves as commercial products The selected polymers include SBS (styrene–butadiene–styrene) and SIS (styrene–isoprene–styrene) triblock copolymers.

Although there are a great number of measurements in the literature, the evaluation of these materials raises a certain difficulty. It has been found that the phase (domain) structure of the samples for testing may be strongly affected by the method of preparation, as, for example the type of solvent used for casting a film [24,25] or the direction of extrusion as found by Odell and Keller [26]. To minimise this difficulty the results selected for study are all from compression moulded test pieces.

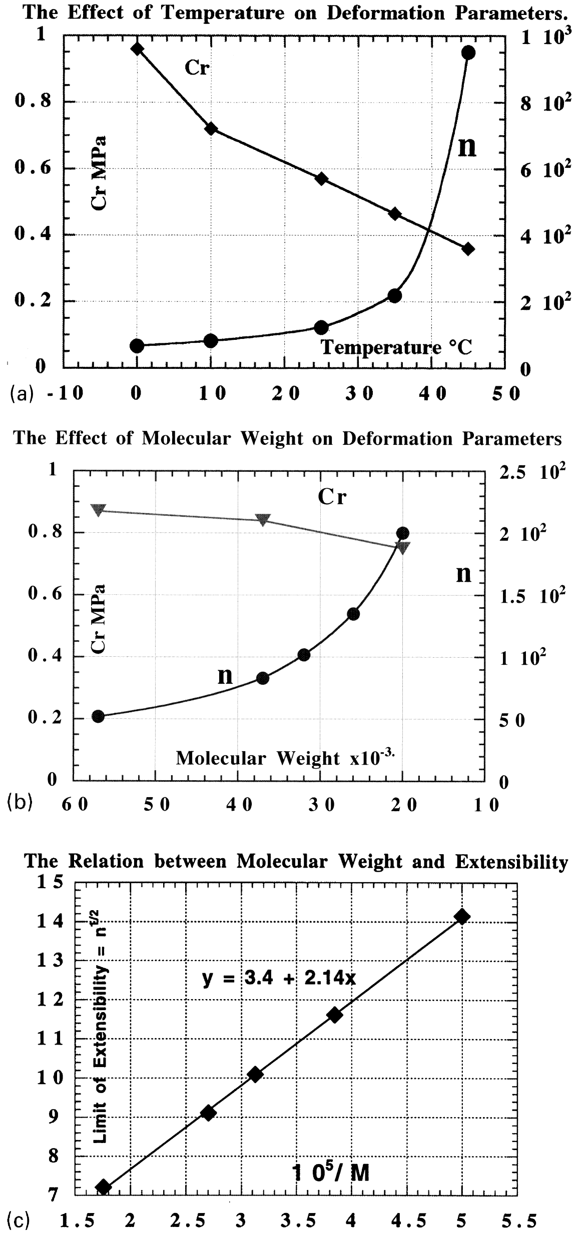

Fig. 5. Factors affecting the parameters of the non-Gaussian equation: (a) the effect of temperature on the non-Gaussian parameters; (b) the effect of molecular weight on the non-Gaussian parameters. Under these conditions both parameters move in opposite senses, corresponding with a softening of the polymer at higher temperatures and lower molecular weights. (c) The effect of molecular weight on the limiting strain. The value of $n^{1/2}$ is linear with 1/M.

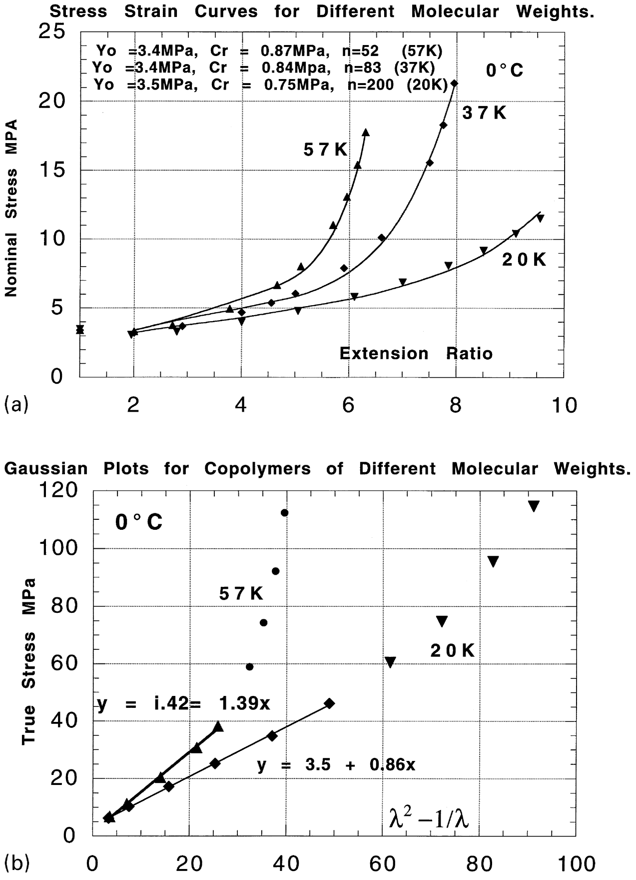

Fig. 6. (a) Lines from Bensason et al. [10] and points calculated from Eq. (5) using the parameters shown. As these polymers have narrow molecular weight distributions weight and number averages should be the same. (b) Gaussian plots for polymers of different molecular weight (0°C). These are the same results as in (a) replotted as true stress–strain curves against the Gaussian function ($\lambda^2 - 1/\lambda$). The increase in n at low molecular weights (Fig. 5(b) and (c)) extends the linear Gaussian range to higher strains. However these lines although apparently quite straight are affected by overlapping effect derived from the limit of extensibility (Fig. 14(a) and (b)) so that the slopes are higher than the values of *Cr* given on Fig. 6(a).

3.5. *The effect of the styrene–butadiene ratio on the tensile properties of SBS copolymers*

The effect of the block weight ratio of SBS triblock polymers on their stress–strain curves has been reported by Morton et al. [27] and Morton [24]. The former prepared a series of copolymers with different compositions in which all the blocks were of uniform size, according to normal practice. In addition some samples were made in which the molecular weight of one of the segments contained units of different length without affecting the overall styrene–diene ratio. To measure the effect of composition SBS copolymers with a 20, 30 and 40% styrene were sythesised and tested. Following the same procedure as before their results are reproduced as continuous lines in Figs. 9 and 10, and fitted by filled points calculated using Eq. (5).

It will be seen that each of the curves can be represented by the model although the closest match is achieved with the 30% styrene copolymer. The parameters of the equation also change in the expected way, i.e. *Cr* increases and *n* decreases with a higher styrene content. Both changes reflect stiffening of the material.

3.6. *The effect of temperature*

The apparently anomalous influence of temperature on the mechanical properties of SBS copolymer has already

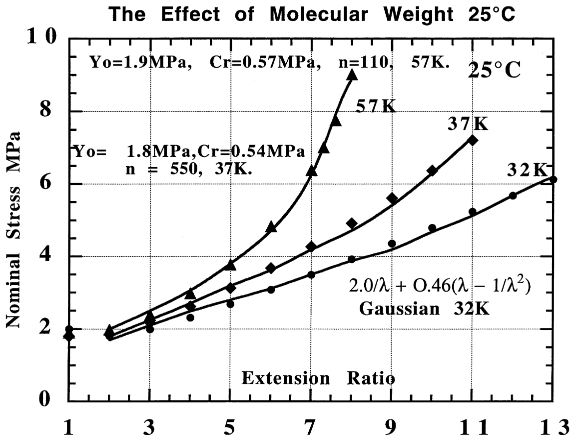

Fig. 7. Very high values of *n* are obtained with the result that the 32 K polymer gives a long Gaussian plot without evidence of a limit of extensibility (parameters shown).

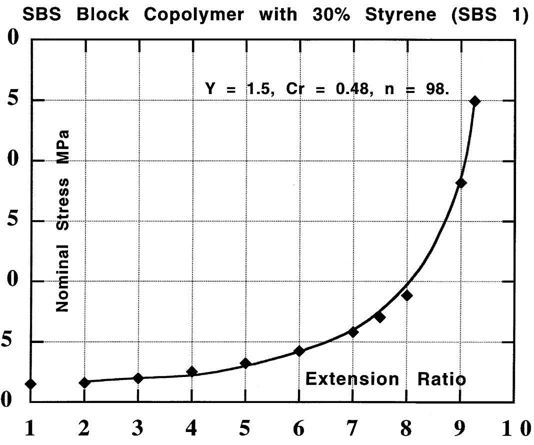

Fig. 9. Stress–strain curve for a block copolymer designated SBS 1 by Morton et al. [27]. The points are calculated from Eq. (5) as before.

been noted. The increase in modulus with temperature is not observed, as the stress required for deformation falls as the temperature is raised [28–31]. The latter, whose results will be quoted here used a commercial SBS copolymer (Kraton 101) with a styrene content of 30.3% by weight. Tensile stress–strain curves were than measured at −40, 0 and 40°C and these are reproduced in Fig. 11 together with points calculated according to Eq. (5). As before, satisfactory fits are obtained which seem to improve at lower temperatures and the parameters *Cr* and *n* move in opposite directions. The value of *Cr* increases and *n* decreases as the temperature is reduced. It is also apparent that *Cr* changes less than *n* and the product $Cr{\cdot}n^{1/2}$ appears to be approximately constant. It is perhaps surprising that in this case there is no evidence of an increase in *Cr* with temperature, as the styrene domains, which supply the equivalent of cross links, should be stable over the temperature range employed.

3.7. Styrene–isoprene–styrene copolymers

Morton et al. [18] prepared 25% styrene SIS copolymers in two ways: one by the regular procedure to give a uniform composition; and a second method where a staged addition procedure was used to provide the isoprene centre block with a hexamodal distribution of molecular weights in a blend with the same overall proportion of styrene. Stress–strain curves for the two materials are given in Fig. 12. Again Eq. (5) gives a series of points which closely follow the line measured for the material with the uniform block structure. However the results for the hexamodal polymer, as shown by the dotted line have stresses well below those for the regular material at high strains. This polymer also has a lower tensile strength so that it is not possible to follow the curve to the point where the existence and value of a limiting strain can be properly demonstrated. It would, of course, have to exceed the value for the regular polymer and this would extend the Gaussian stage.

It may be noted that the even for the regular isoprene copolymer the value of the limiting strain determined by *n* is considerably greater than that for an equivalent SBS copolymer.

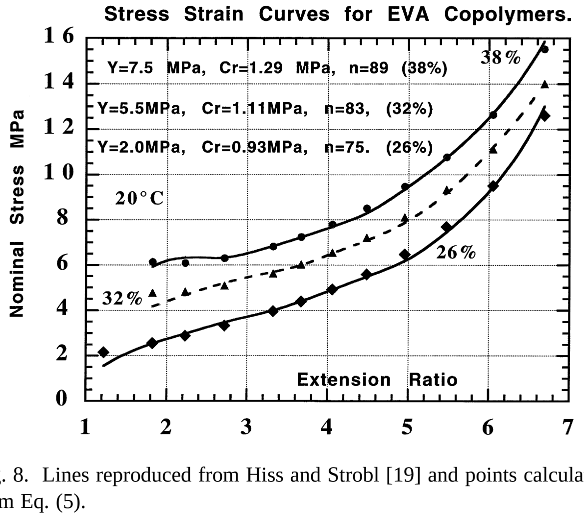

Fig. 8. Lines reproduced from Hiss and Strobl [19] and points calculated from Eq. (5).

4. Discussion

4.1. The use of the non-Gaussian and slip-link equations to model large deformations

In the foregoing presentation it has been shown that the non-Gaussian rubber elasticity equation can be used successfully to model large tensile strains in several thermoplastic rubbers when an undefined yield stress is introduced as a disposable constant. With the ultra low density polyethylenes Bensason et al. [10] have demonstrated that the rather complex ‘‘slip-link’’ equation given in Appendix B, which employs an additional physically defined parameter, can be used to model the whole stress–strain curve including the initial stages. Both theories generate a limit of extensibility which relates to α in the slip-link theory and to *n* in

Table 3
Specification of vinyl acetate copolymers

Grade	VA (% by weight)	Melt index (gm.10 min)	Crystallinity (%, [19])
Exxon 0012	12.0	0.30	38
Exxon 0018	17.5	0.37	32
Exxon 00328	27.0	3.0	26

the non-Gaussian equation ($n^{1/2} = \lambda_{\max}$). Both equations revert to the conventional Gaussian forms under certain conditions, i.e. for the non-Gaussian equation when n and therefore $\lambda_{\max}$ are very large, and for the slip-link equation, when the parameters η and α approach zero. The condition $\alpha = 0$ is essentially equivalent to n becoming infinite. The slip-link equation has the advantage of offering a comprehensive coverage of the whole deformation process while, however, the non-Gaussian treatment offers a rather simple semi-empirical relation describing the large deformation process in terms of intuitively intelligible parameters. Particularly the limiting strain represented by $n^{1/2}$ appears to represent a clear and measurable physical entity.

In their discussion Bensason et al. [10] point out that the slip links model a yield like process which they illustrate by the reversible detachment and attachment of crystallisable chain segments. Such rearrangements could help to increase configurational entropy of the polymer chains in the early stages of deformation and so to reduce the measured modulus. However, if the detachments were permanent or if some of the crystals were broken up there would be a difference between the first and subsequent deformations of the same test piece, which would cease to be truly reversible.

Measurements of this type have not, so far, been recorded for the ultra low density polyethylenes, but the effect is well known with the SBS block copolymers especially with high proportions of styrene. For example at 40% styrene content (by weight) Fischer and Henderson [29] observed marked hysteresis effects while Smith and Dickie [31] with a 30% styrene polymer found a significant softening after the first one or two deformations while after 3–4 cycles the process became reversible. Even with only 20% styrene small hysteresis effects were observed by Childers and Krauss [32].

In any case, as pointed out by Bensason et al. [10], as crystallinity increases in the margin between Type I and II polyethylenes [20], lamellar crystalline structures appear and the characteristic feature of a yield process are observed.

More generally the question arises as to how entropy changes are to be introduced into the theory of unconventional rubbers. Bensason et al. propose, very convincingly that the changes of elasticity with temperature which they observe are related to demonstrable changes in crystallinity. However it seems more difficult to explain in this way the changes observed by Smith and Dickie for SBS between −40 and +40°C although it should be noted that the molecular weight of their end blocks (11 000) was well below the ‘‘entanglement molecular weight’’ of polystyrene, or the molecular weight of the material as normally used for moulding purposes.

It is felt that the results obtained encourage the evaluation of different rubber entropy equations for use with unconventional rubbers and hard thermoplastics as practised by Boyce and Arruda [38] for glassy polymers, and for thermoplastic rubbers including the ultra low density polyethylenes by Bensason et al. [10]. The results can then be compared

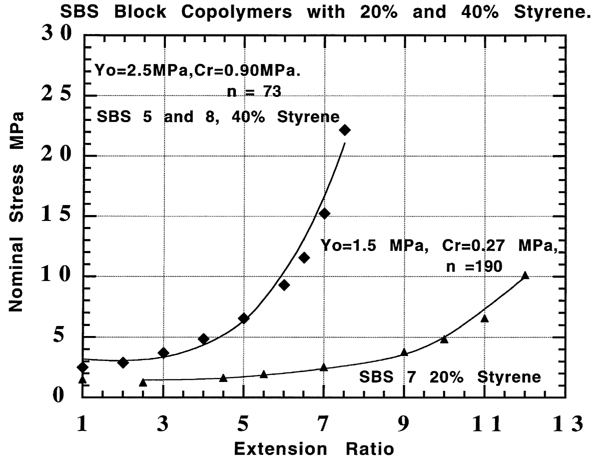

Fig. 10. The top curve represents the line drawn by Morton et al. [27] through the results for the two copolymers SBS 5 and 8, both with 40% styrene but with different overall molecular weights. The bottom curve was also reproduced from Ref. [27]. All the points were calculated from Eq. (5).

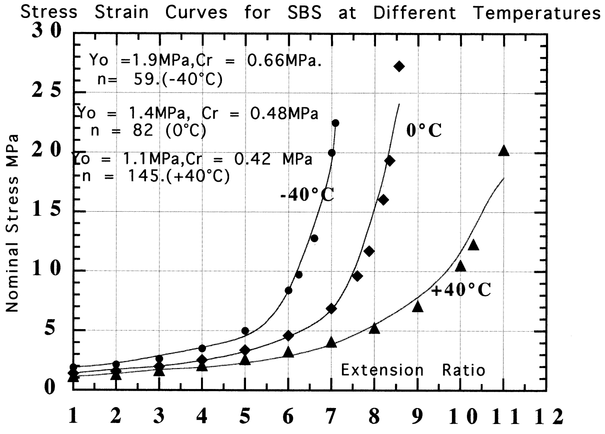

Fig. 11. From the work of Smith and Dickie [31]. The polymer is a commercial product Kraton 101 with a measured styrene content of 30.3% by weight. Large changes in both n and Cr occur at quite low temperatures.

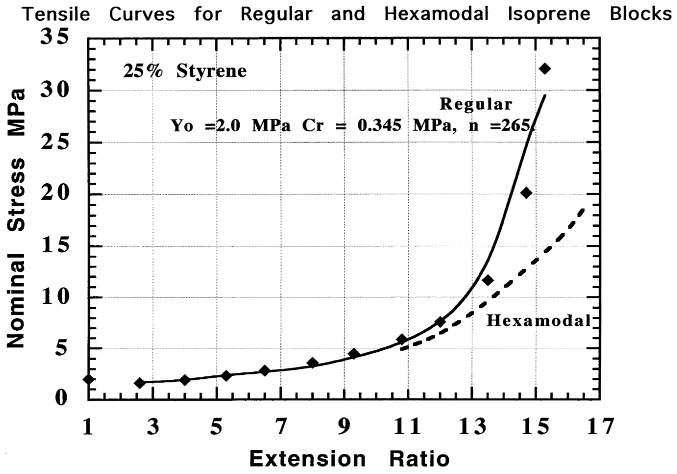

Fig. 12. The isoprene centre block gives a higher values of *n* than the SBS copolymers. The dotted line represents a copolymer with the same average proportion of isoprene but with a herogeneous centre block made by a six stage polymerisation procedure [27].

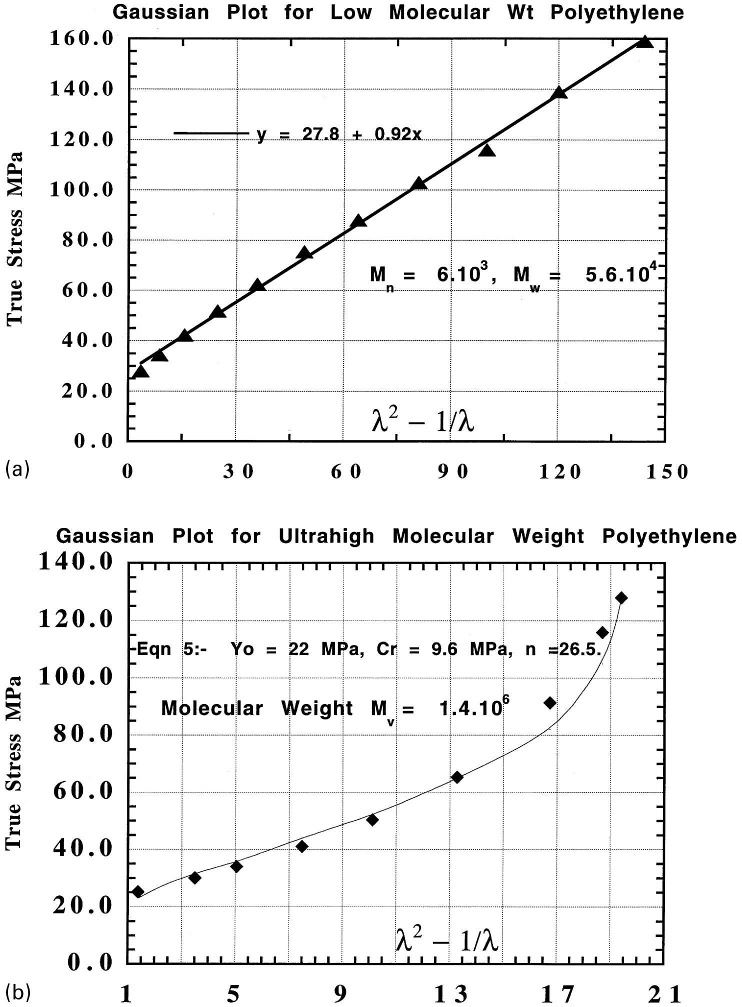

Fig. 13. (a) Gaussian plot for a high density low molecular weight polyethylene. This material gives a nearly straight line up to $\lambda = 12$, ($M_n = 6 \times 10^3$, $M_w = 56 \times 10^3$, density = 0.96); (b) most medium and high density polyethylene show long linear regions in a Gaussian plot but the ultrahigh molecular weight material has marked curvature and which can only be fitted by the non-Gaussian equation. ($M_n = 3 \times 10^4$, $M_v = 1.4 \times 10^6$ (near to M_w), density 0.93, Branching 1.8/1000 C atoms). (Data from Meinel and Peterlin [34,35] and Ref. [13].)

with those from the conventional Gaussian and non-Gaussian equations used here.

4.2. Factors affecting the deformation parameters of the non-Gaussian model

4.2.1. Effect of crystallinity

According to rubber elasticity theory, from which it is derived, the quantity *n* in the non-Gaussian equation represents the number of flexible connections between cross links, while *Cr* is equated with *NkT* where *N* is the number of cross links. Thus *nN* should be constant and equal the total number of flexible units in the system, as pointed out by Arruda et al. [33] for glassy polymers.

For semi-crystalline polymers the constancy of *nN* is hardly to be expected but if, for instance, the material becomes softer it would be logical to expect the two parameters to change in opposite senses, i.e. for *N* to decrease and *n* to rise. For the most part this seems to apply to the present results but when the parameters are plotted against the percent crystallinity for the polyethylenes the expected trends occur only up to a crystallinity of 30%. Above this level *n* appears to increase again as also is the case for the vinyl acetate copolymers (measured by method C). This crystallinity level corresponds to the middle of the range suggested for Type II polymers and marks the transition from rubberlike to solid polymers [20]. With the polymers described in Fig. 3 *n* does not reach a very high value, but if the trend were to continue at higher crystallinities the stress–strain curves would assume an increasingly Gaussian form. There is now extensive evidence that this is indeed the case and many examples of linear Gaussian plots have been reported by G'Sell and Jonas [7], Haward [13] and Hillmansen et al. [23]. Further, experiments by Meinel and Peterlin [34,35] with low molecular weight high-density polyethylene and with ultrahigh molecular weight medium density polymer illustrate this point. True stress–strain curves with the low molecular weight material give a linear Gaussian plot even up to a λ value as high as 12 (Fig. 13(a)). With the ultrahigh molecular weight material marked curvature is found in a similar plot which can only be represented by the non-Gaussian Eq. (5) with high values of *Cr* and low values of *n* (Fig. 13(b)). This reflects the effect of molecular weight on *n* (discussed later).

If the conventional rubber elasticity formula [36] is used to estimate the molecular weight (M_e) of the active chains between cross links, we obtain

$$M_e = \rho RT/G = \rho RT/Cr.$$

We can derive the number of carbon atoms associated with a crystalline cross link as $M_e c/14\rho$, where c is the crystallinity in g/cc and ρ the density in the same units (as in Ref. [10]). Then from Fig. 3, neglecting the small intercept, we obtain $Cr = 4.9c$ MPa. This leads to a value of 35 C atoms per cross link which corresponds to a length of 44 a.u. [37] somewhat higher than the 19–30 a.u. proposed by Bensason et al. [10]. However the good linearity of the plot of *Cr* against *c* would suggest that this quantity may not vary with the comonomer content to the extent they propose.

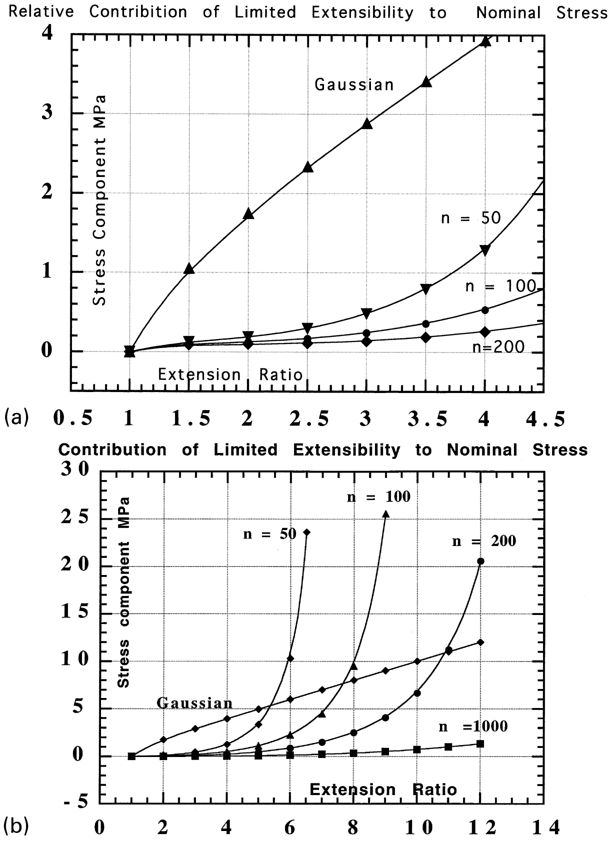

Fig. 14. The figure shows the contribution of a Gaussian stress (Cr = 1 MPa) and the additional stress due to the inextensibility factor introduced by the non-Gaussian equation with different values of n: (a) at low strains; (b) at high strains.

4.2.2. Effect of molecular weight

Bensason et al. included the effect of molecular weight in their study of the deformation of low crystalline polyethylenes. However, in comparing these results with other polyethylenes it is important to appreciate that the new ''Insite'' polymers are reported to have narrow molecular distributions so that the number and weight averages are approximately the same and it is not necessary to represent molecular weight by two figures. This may complicate comparisons with other products especially where molecular weight differences are small and distributions wide though it does not, of course, affect the significance of the results reported in Ref. [10].

The influence of molecular weight on the parameters of the non-Gaussian equation at 0°C has been presented in Fig. 6(b) and (c). The small differences in the values of *Cr* at low extensions made it impossible to separate some of the curves, so that only three full graphs could be plotted and even then they were subject to significant error at low strains. In their discussion of molecular weight effects, Bensason et al. concentrate on the measurements of their cross link modulus (N_c) at higher temperatures in order to avoid overlap due to high values of the inextensibility factor α. That this overlap can be very significant is shown in Fig. 6(b) where Gaussian plots are displayed to show how the length of initial linear section increases with higher values of *n* when the full non-Gaussian treatment is not used When Eq. (5) is applied lower *Cr* values of are found from which the overlap is believed to have been removed. So the slight upward trend of *Cr* with molecular weight may be significant in spite of the errors involved.

The measurement of five complete curves at 0°C makes it possible to derive a dependence of *n* on molecular weight [Fig. 5(c)] which is shown to follow a Flory [38] reciprocal plot. Interestingly the slip-link treatment leads to a similar relationship for their cross link modulus N_c at higher temperatures. Both results point to the importance of chain ends in determining mechanical properties. Finally the fact that at low molecular weights temperatures above 0°C *n* becomes very large making it possible to show from experimental results that under these conditions the stress–strain curve can indeed take on a fully Gaussian form as show in Fig. 7.

This feature may be directly illustrated from the model as in Fig. 14(a) and (b). In these graphs the yield stress is assumed to be either small or zero and the inextensibility effect is isolated by subtracting the Gaussian contribution from the calculated stress, i.e. Eq. (4) is subtracted from Eq. (5). The results are plotted for lower values of λ Fig. 14(a) and for λ values up to 12 in Fig. 14(b). Clearly, if *n* is not very high the value of *Cr* calculated up to extension ratios no higher than 5 will be affected by overlap from the inextensibility factor (as shown in Fig. 7). However when $n = 1000$ its influence on the deformation stress is negligible for $\lambda < 7$. When the yield stress is small, it may also be noted that when quantity *f/Cr* is plotted against λ the resulting curve is entirely determined by the parameter n.

5. Conclusions

1. The application of a conventional elasticity equation can be simplified by the introduction of a Pade approximation [14] for the inverse Langevin function.
2. When a small, initial yield stress is added the modified equation may be used to model stress–strain curves for thermoplastic elastomers above extension ratios of 1.5–2.0. Ultra low-density polyethylenes, ethylene vinyl acetate copolymers and SBS block copolymers have been treated successfully.
3. The three parameters of the equation comprise two physical entities, an initial modulus *Cr* and an ultimate extension ratio $n^{1/2}$.
4. The polyethylene and the SBS polymers have lower moduli (*Cr*) at higher temperatures. With the polyethylenes this decrease correlates with reduced crystallinity but with the SBS copolymer it occurs at temperatures where the styrene domains should be stable.
5. When *n* becomes large, the equation becomes Gaussian in accordance with the literature [7].
6. The quantity $n^{1/2}$ has been found to follow a Flory type dependence on 1/M.

Acknowledgements

The author is indebted to Prof J.H.R. Clarke and Mr D. Radcliffe for assistance in computation and to Prof A.G. Thomas and to Dr D.J. Meier for much helpful advice.

Appendix A

In his presentation of Eq. (1) Treloar [7] notes that at low values of λ it approximates to a gaussian form. He also describes a treatment based on an assembly of chains following an inverse Langevin expression for entropy, in the form of the series given below [7, eqn 6.22].

$$f = NkT\left(\lambda - \frac{1}{\lambda^2}\right)\left\{1 + \frac{3}{25n}\left(3\lambda^2 + \frac{4}{\lambda}\right) + \frac{297}{6125n^2}\right.$$
$$\times\left(5\lambda^4 + 8\lambda + \frac{8}{\lambda^2}\right) + \frac{12\,312}{2\,205\,000n^3}$$
$$\times\left(35\lambda^6 + 60\lambda^3 + 72 + \frac{64}{\lambda^3}\right) + \frac{126\,117}{693(673\,750)n^4}$$
$$\left.\times\left(630\lambda^8 + 1120\lambda^5 + 1440\lambda^2 + \frac{1536}{\lambda} + \frac{1280}{\lambda 4}\right) + \ldots\right\} \tag{A.1}$$

This equation assumes a Gaussian form when *n* is large.

Appendix B

The Advanced Rubber Elasticity Equation used by Bensason et al. [10].

The equation is quoted below.

$$\frac{F}{kT} = \frac{1}{2}N,\left(\sum_i\left[\frac{\lambda_i^2(1-a^2)(1+\eta)}{(1-a^2\sum_i\lambda_i^2)(1-\eta\lambda_i^2}\right.\right.$$
$$\left.\left.+\log(1+\eta\lambda_i^2\right] + \log(1-a^2\sum_i\lambda_i^2\right)$$
$$+\frac{1}{2}N_c\left(\frac{\sum_i\lambda_i^2(1-a^2)}{(1-a^2\sum_i\lambda_i^2} + \log(1-a^2\sum_i\lambda_i^2\right) \tag{B.1}$$

The four parameters are as follows—the density of cross linked chains $N_{c,}$ the density of slip links N_s, the slippage parameter η and the inextensibility parameter α.

The condition $\alpha = 0$ is equivalent to n becoming infinite in the non-Gaussian equation. Under these conditions the second term becomes Gaussian.

References

[1] Kramer EJ, Berger LL. Adv Polym Sci 1990;91:2.
[2] Donald AM, Kramer EJ. J Polym Sci (Phys.) 1982;20:899.
[3] Mckechnie JJ, Haward RN, Brown D, Clarke JHR. Macromolecules 1993;26:198.
[4] Haward RN, Thackray G. Proc R Soc Lond 1968;303:453.
[5] Boyce MC, Parks DM, Argon A. Mech Mater 1988;715:35.
[6] Boyce MC, Haward RN. In: Haward RN, Young RJ, editors. The physics of glassy polymers, 2nd edn. London: Chapman and Hall, 1997 ch. 5.
[7] Treloar LRG. The physics of rubber elasticity. 3. Oxford: Clarendon Press, 1975.
[8] Sinclair SB, Wilson RB. Chemistry and industry. 1994:862.
[9] Legge NR, Holden G, Schroeder HE, editors. Thermoplastic elastomers, Munich: Carl Hanser, 1987.
[10] Bensason S, Stepanov EV, Chum S, Hiltner A, Baer E. Macromolecules 1997;30:2436.
[11] Ball RC, Doi M, Edwards SF, Warner M. Polymer 1981;22:1010.
[12] Thirion P, Weil T. Polymer 1984;25:609.
[13] Haward RN. Macromolecules 1993;26:5860.
[14] Cohen A. Rheol Acta 1991;30:270.
[15] Walker N, Haward RN, Hay JN. J Mater Sci 1981;16:817.
[16] G'Sell C, Jonas JJ. J Mater Sci 1979;14:583.
[17] G'Sell C, Jonas JJ. J Mater Sci 1981;16:1956.
[18] Hope PS, Ward IM, Gibson AG. J Mater Sci 1980;15:2207.
[19] Hiss R, Strobl G. Deformation, Yield and Fracture of Polymers Conference, Cambridge. Insitutute of Materials, London SW1B 5DB, 1997:439.
[20] Bensason S, Minick JS, Chum S, Hiltner A, Baer E. J Polym Sci (Phys) 1996;34:1301.
[21] Bensason S, Nazarenko S, Chum S, Hiltner A, Baer E. Polymer 1997;38:3513.
[22] Bensason S, Nazarenko S, Chum S, Hiltner A, Baer E. Polymer 1997;38:3913.
[23] Hillmansen S, Hobbeika S, Haward RN, Leevers PS. Polym Engng Sci 1999: in press.
[24] Morton M. In: Legge NR, Holden G, Schroeder HE, editors. Thermoplastic elastomers, Munich: Carl Hanser, 1987 Ch. 4.
[25] Uchida T, Soen T, Inoue T, Kawai H. J Polym Sci 1972;A2.10:101.
[26] Odell JA, Keller A. Polymer Engng Sci 1977;17:544.
[27] Morton M, McGrath JE, Juliano PC. J Polym Sci 1969;C26:99.
[28] Kaelble DH, Cirlin EH. J Polym Sci 1973;C43:131.
[29] Fischer E, Henderson JF. Rubber Chem Tech 1967;40:1373.
[30] Fischer E, Henderson JF. J Polym Sci 1969;C26:152.
[31] Smith TL, Dickie RA. J Polym Sci 1969;C26:163.
[32] Childers CW, Kraus G. Rubber Chem Tech 1967;40:1183.
[33] Arruda EM, Boyce MC, Jayachandran R. Mech Mater 1995;19:193.
[34] Meinel G, Peterlin A. J Polym Sci 1971;A29:67.
[35] Meinel G, Peterlin A. Eur Polym J 1971;7:657.
[36] Ferry JD. Viscoelastic properties of polymers. 3rd edn. New York: Wiley, 1980 (see also Ref. [7]).
[37] Vincent PI. Polymer 1972;13:558.
[38] Flory PJ. Ind Engng Chem 1946;38:417.