BUTTERWORTH HEINEMANN

Polymer Vol. 36 No. 2, pp. 309–313, 1995

0032-3861/95/$10.00+0.00

Non-Gaussian stress–strain constitutive equation for crosslinked elastomers

G. Spathis
Department of Engineering Science, Section of Mechanics, National Technical University of Athens, 5 Heroes of Polytechnion Avenue, GR-157 00 Athens, Greece
(Received 10 January 1994)

A stress–strain equation is studied which uses a non-Gaussian statistical mechanics model for large deformation of crosslinked rubbers. The formulation is based on the work introduced by Doi and Edwards for the description of polymer dynamics in a fixed network. The resulting constitutive equation is applied in the entire network of elastomers. Uniaxial and biaxial tensile and compressive experiments are explained in detail. Comparison with other theoretical work reveals that the present model could be applied equivalently in any kind of physical or chemical network junction.

(Keywords: rubber elasticity; constitutive equation; stress–strain tests)

INTRODUCTION

The rubber elasticity approach includes a great variety of descriptions, models and concepts. Statistical mechanics based on Gaussian distribution for the end-to-end distance of a chain, constitutes a remarkable interpretation of rubber behaviour under small deformations[1–4]. This description, however, fails in the case of large extension, where non-Gaussian statistics should be employed[5]. In addition to such an improvement, a more accurate statistical theory is necessary, accounting for all the network chains. Following this perspective, James and Guth[6] developed a model separating the entire network into three independent sets of single chains, oriented in three orthogonal directions. More detailed studies have followed this approach, where the actual spatial orientation chain distribution is taken into account. Treloar and Riding[7] and Wu and Van Der Giessen[8] have developed a rubber elasticity theory based on a full network description. According to their consideration, a number of initially randomly oriented chains proved to be determined by a balance equation in orientational space. By using a non-Gaussian statistical mechanics approximation, a general formulation network model has been established, which is valid for any type of deformation and rubber. The entire network approach achieved better experimental verification. This fact prompted many researchers to suggest a further improvement of the theory.

This improvement requires a better understanding of the role of network defects in rubber-like materials. The most favourable topological obstructions of elastomeric networks are entanglements, which are often related to some discrepancies observed in the predictions of classic statistical theory[9,10]. These defects are largely accepted to be mechanically effective, and they are used to provide a large value of the modulus in crosslinked rubbers. In many cases, entanglements are treated as physical crosslink junctions, in constructing various separated constitutive equations[11–15].

In the present study, a stress–strain equation will be developed, describing large extensions in crosslinked elastomers. Our formulation is based on the work of Doi and Edwards[16] concerning the description of polymer dynamics in a fixed network. The idea of a chain trapped in a tube-like region, constituted from the topological constraints, is attractive for relaxation phenomena of polymer chains in uncrosslinked systems. However, this concept is applied primarily for studying the problem of rubber elasticity[13,17].

The present analysis will be confined to stress response of chains participating in the rubber network, so we will eliminate relaxation phenomena which originate from the disengagement of a linear chain trapped in a tube. The non-Gaussian statistics of inverse Langevin approximation will be used to calculate the microscopic stress developed on polymer molecules. The resulting constitutive equation is applied in the entire network of rubbers. Various modes of deformation, such as uniaxial and biaxial extension or uniaxial and plane-strain compression, will be described in detail. Comparison with other theoretical work reveals that certain experimental tests are explained without any suggestion for the specific role of network defects in rubber-like materials.

THE CONSTITUTIVE EQUATION

The following formulation is based on the assumption that the long molecules of a crosslinked rubber are constrained within a tube-like region. Owing to topological constraints, the thermal motion of the segments is limited over short distances. A chain in such a rubber is shown schematically in *Figure 1*. At equilibrium the tube itself is considered as a random coil. The segments of the chain wriggle around the axis of the tube and are called the primitive chain. To denote a point on the primitive chain, Doi and Edwards used the contour length S, measured from the chain end. If $\boldsymbol{R}(s)$ is the position vector of segment S, the derivative in respect of

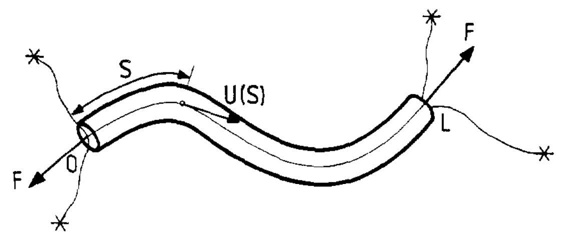

Figure 1 Schematic picture of a network chain trapped in a tube-like region

S is the unit vector directed tangentially to the primitive chain:

$$u(s)=\frac{\partial}{\partial s}R(s) \quad (1)$$

The total contour length is denoted by L, following an elementary argument. A microscopic expression for the stress tensor can be obtained[16]:

$$\sigma_{\alpha\beta}=\frac{C}{N}\left\langle \int_0^{L} \mathrm{d}sF(s)\, u_\alpha(s)u_\beta(s)\right\rangle - p \quad (2)$$

where the angle brackets denote ensemble average, C is the number of segments per unit volume, N is the number of segments per chain, $F(s)$ is the tensile force acting along the primitive chain, $u_\alpha(s)$, $u_\beta(s)$ are components of the unit vector, and p is an indeterminate hydrostatic pressure. If Δs denotes the length of a line segment on the primitive chain, its mean value is given by:

$$\overline{\Delta s}=bL\left(\frac{F(s)b}{k_B T}\right) \quad (3)$$

where L is the Langevin function, b is Kuhn's statistical segment, T is the absolute temperature and k_B is the Boltzmann constant. Multiplying this expression by the number of segments per chain, we obtain the mean value of the contour length $\langle L\rangle$:

$$\langle L\rangle = N\overline{\Delta s}=NbL\left(\frac{F(s)b}{k_B T}\right) \quad (4)$$

Doi and Edwards assumed that the tensile force along the chain is independent of S, because local imbalances in the segment density are adjusted in a very short time. In this case the tensile force in the deformed state is given by:

$$F=\frac{k_B T}{b}L^{-1}\left(\frac{\langle L\rangle}{Nb}\right) \quad (5)$$

From equations (2) and (5) the stress tensor takes the form:

$$\sigma_{\alpha\beta}=\frac{C}{N}\frac{k_B T}{b}\left\langle L^{-1}\left(\frac{\langle L\rangle}{Nb}\right)\int_0^{L} \mathrm{d}s u_\alpha(s)u_\beta(s)\right\rangle - p \quad (6)$$

This formula depends on two quantities, the contour length L and the orientation $u(s)$. Supposing that deformation is affine, the primitive chain is deformed in the same way as macroscopic deformation. If E denotes the deformation gradient, the position vector of the primitive chain is displaced as:

$$R'(s)=ER(s) \quad (7)$$

Since the distribution of the unit vector is isotropic in the undeformed state, Doi and Edwards suppose that the average change of contour length L is:

$$\langle L\rangle=\alpha(E)\langle L_0\rangle$$

where

$$\alpha(E)=\langle|Eu|\rangle_0=\int\frac{\mathrm{d}u}{4\pi}|Eu| \quad (8)$$

is the average over isotropic state and L_0 is the contour length in the undeformed state.

The change of the orientation of the primitive path is denoted by the orientational tensor:

$$Q_{\alpha\beta}(E)=\langle u_\alpha(s)u_\beta(s)\rangle \quad (9)$$

Considering the probability distribution function $f(u,s)$ of the tangent vector $u(s)$ after deformation, Doi and Edwards obtain the following formula for $Q_{\alpha\beta}(E)$:

$$Q_{\alpha\beta}=\int_0^{L}\mathrm{d}u\, u_\alpha(s)u_\beta(s)f(u,s)=\left\langle\frac{(Eu)_\alpha(Eu)_\beta}{|Eu|}\right\rangle_0\frac{1}{\langle|Eu|\rangle_0} \quad (10)$$

Combining equations (8) and (9), the stress tensor (equation (6)) takes the form:

$$\sigma_{\alpha\beta}=\frac{C}{N}\frac{k_B T}{b}\left[L^{-1}\left(\frac{\langle L_0\rangle\,\alpha(E)}{Nb}\right)\right]\int_0^{\langle L\rangle}\mathrm{d}s\langle u_\alpha(s)u_\beta(s)\rangle - p$$

$$=\frac{C}{N}\frac{k_B T}{b}L^{-1}\left(\frac{\langle L_0\rangle\alpha(E)}{Nb}\right)\langle L_0\rangle\,\alpha(E)Q_{\alpha\beta}(E)-p \quad (11)$$

This equation, a part of the inverse Langevin approximation, has a similar form to the corresponding expression derived by Marrucci[11] for the entangled chains. It is worthwhile to notice that the deformed contour length $\langle L_0\rangle\alpha(E)$ and the orientational tensor $Q_{\alpha\beta}(E)$ are grouped separately from the applied force. This fact is a direct result of the assumption that the force acting on each segment tangentially along the primitive chain is constant.

Marrucci supposed equal tensile forces of successive entanglement points of the same chain. This assumption provided the above-mentioned separation but resulted in different expressions for the entangled chain, in contrast to other network junctions. In conclusion, we are convinced that Marrucci's equation does not constitute a discrete form for the physical entanglements. These results are in agreement with the experimental tests presented by Gottlied and Gaylord[18], where several entanglement models have been examined and predict uniaxial stress–strain response for crosslinked polymers. As they suggest, entangled networks cannot be accurately described with the slip link model of Doi and Edwards[16] or the similar approximations by Marrucci[11] and Graessly[15].

Equation (11) could be modified to a more simplified form if a relation between the undeformed mean primitive length $\langle L_0\rangle$ and the Rouse chain Nb^2 is estimated. Applying equation (11) in the case of shear deformation for small shear strains γ, $Q_{\alpha\beta}(\gamma)$ and $\alpha(\gamma)$ are easily calculated:

$$\alpha(\gamma)\cong 1 \quad \text{and} \quad Q_{\alpha\beta}(\gamma)\cong\frac{4}{15}\gamma$$

Thus equation (11) becomes:

$$\sigma_{\alpha\beta}=\frac{4}{15}\frac{C}{N}\frac{3k_{\mathrm{B}}T}{Nb^2}\langle \mathrm{L_0}\rangle^2\gamma \qquad (12)$$

In small deformation, however, the Gaussian chain takes the following form under shear strain:

$$\sigma_{\alpha\beta}=\frac{C}{N}k_{\mathrm{B}}T\gamma \qquad (13)$$

Equating equations (12) and (13):

$$\frac{\langle \mathrm{L_0}\rangle}{bN}=\left(\frac{15}{12}\right)^{1/2} \qquad (14)$$

and substituting this expression into equation (11) we obtain:

$$\sigma_{\alpha\beta}=C^{\mathrm{R}}\sqrt{N}\left(\frac{15}{12}\right)^{1/2}L^{-1}\left[\frac{\alpha(E)}{\sqrt{N}}\left(\frac{15}{12}\right)^{1/2}\right]\alpha(E)Q_{\alpha\beta}(E)-p \qquad (15)$$

where $C^{\mathrm{R}}=Ck_{\mathrm{B}}T/N$. Equation (15) is the constitutive equation of the stress tensor in crosslinked rubber as derived by the assumed model. Further on, the prediction of equation (15) will be considered for various types of deformation. Experimental results will be examined and compared with the constitutive equation derived by Wu and Van Der Giessen[8].

Biaxial and uniaxial tensile extension

To confirm the above-mentioned model, equation (15) will be applied first for biaxial tensile stretching. The components of the associated unit direction vector $\boldsymbol{u}$ in the current state are expressed in terms of spherical polar angles ϑ,φ:

$$\boldsymbol{u}_x=\sin\vartheta\cos\varphi, \qquad \boldsymbol{u}_y=\sin\vartheta\sin\varphi, \qquad \boldsymbol{u}_z=\cos\vartheta \quad (16)$$

If a biaxial extension is applied to rubber material in the xy plane, the deformation gradient tensor E is:

$$E=\begin{bmatrix}\lambda & 0 & 0\\ 0 & \lambda & 0\\ 0 & 0 & \dfrac{1}{\lambda^2}\end{bmatrix} \qquad (17)$$

Quantities $\alpha(E)$ and $Q_{\alpha\beta}(E)$ are analytically calculated as follows:

$$\alpha(E)=\alpha(\lambda)=\langle|E\boldsymbol{u}|\rangle_0=\frac{1}{4\pi}\int \mathrm{d}\boldsymbol{u}\left[\lambda^2\boldsymbol{u}_x^2+\lambda^2\boldsymbol{u}_y^2+\frac{1}{\lambda^2}\boldsymbol{u}_z^2\right]^{1/2}$$

$$=\frac{1}{4\pi}\int_0^{\pi}\int_0^{2\pi}\left[\lambda^2\sin^2\vartheta+\frac{1}{\lambda^2}\cos^2\vartheta\right]^{1/2}\sin\vartheta\,\mathrm{d}\vartheta\,\mathrm{d}\varphi$$

$$=\frac{1}{2\lambda^2}+\frac{\lambda^4}{2\sqrt{\lambda^6-1}}\sin^{-1}\sqrt{\frac{\lambda^6-1}{\lambda^6}} \qquad (18)$$

$$Q_{\alpha\beta}(E)=\left\langle\frac{(E\boldsymbol{u})_\alpha(E\boldsymbol{u})_\beta}{|E\boldsymbol{u}|}\right\rangle_0\frac{1}{\langle E\boldsymbol{u}\rangle_0} \qquad (19)$$

For the diagonal components of this tensor we will calculate the quantities

$$\left\langle\frac{(E\boldsymbol{u})_x(E\boldsymbol{u})_x}{|E\boldsymbol{u}|}\right\rangle_0=\frac{1}{4\pi}\int_0^{\pi}\int_0^{2\pi}\lambda^4\frac{\sin^2\vartheta\cos^2\varphi}{[\lambda^6\sin^2\vartheta+\cos^2\vartheta]^{1/2}}\sin\vartheta\,\mathrm{d}\vartheta\,\mathrm{d}\varphi$$

$$\left\langle\frac{(E\boldsymbol{u})_z(E\boldsymbol{u})_z}{|E\boldsymbol{u}|}\right\rangle_0=\frac{1}{4\pi}\int_0^{\pi}\int_0^{2\pi}\frac{1}{\lambda^2}\frac{\cos^2\vartheta}{[\lambda^6\sin^2\vartheta+\cos^2\vartheta]^{1/2}}\sin\vartheta\,\mathrm{d}\vartheta\,\mathrm{d}\varphi \qquad (20)$$

To eliminate the indeterminate hydrostatic pressure P from equation (15) the following quantity is calculated:

$$f(\lambda)=\alpha(E)[Q_{xx}(E)-Q_{zz}(E)]$$

$$=\left[\frac{1}{\lambda^6-1}\frac{2\lambda^2+1}{2\lambda^2}+\frac{\lambda^4}{\sqrt{(\lambda^6-1)^3}}\left(\frac{2\lambda^6-5}{2}\right)\sin^{-1}\sqrt{\frac{\lambda^6-1}{\lambda^6}}\right] \qquad (21)$$

From equations (15), (18) and (21) the tensile stress is given by:

$$\sigma_{\mathrm{T}}=\sigma_{xx}-\sigma_{zz}=C^{\mathrm{R}}\sqrt{N}\left(\frac{15}{12}\right)^{1/2}L^{-1}\left[\frac{\alpha(\lambda)}{\sqrt{N}}\left(\frac{15}{12}\right)^{1/2}\right]f(\lambda) \qquad (22)$$

For uniaxial elongation, the tensile stress is given by a similar equation where explicit expressions for $\alpha(\lambda)$ and $f(\lambda)$ are given by Marrucci[11]:

$$\alpha(\lambda)=\frac{1}{2}\lambda\left(1+\frac{\sinh^{-1}\sqrt{\lambda^3-1}}{\lambda^3\sqrt{\lambda^3-1}}\right) \qquad (23)$$

$$f(\lambda)=\frac{\lambda^3+\frac{1}{2}}{\lambda^3-1}\left(1+\frac{\sinh^{-1}\sqrt{\lambda^3-1}}{\lambda^3\sqrt{\lambda^3-1}}\right)\left(1-\frac{4\lambda^3-1}{2\lambda^3+1}\frac{\sinh^{-1}\sqrt{\lambda^3-1}}{\lambda^3\sqrt{\lambda^3-1}}\right)$$

Figures 2a and *b* include experimental results for uniaxial and biaxial tension of a natural rubber gum as reported by James *et al.*[19]. In the same plots the results of equation (22) and the full network model introduced by Wu and Van Der Giessen[8] are also shown. According to their concern, the principal stresses are given by the following expression:

$$\sigma_i=C^{\mathrm{R}}\sqrt{N}\int_0^{\pi}\int_0^{2\pi}C(\vartheta,\varphi,\lambda_i)L^{-1}\left(\frac{a}{\sqrt{N}}\right)am_i^2\sin\vartheta\,\mathrm{d}\vartheta\,\mathrm{d}\varphi-p \qquad (24)$$

where $C(\vartheta,\varphi,\lambda_i)=\frac{1}{4\pi}a^3(\vartheta,\varphi,\lambda_i)$ is the spatial distribution of the chain orientations for an arbitrary three-dimensional deformation, a is the stretch of a single chain, and m_i are the components of the unit direction vector:

$$a^{-2}=\sum_1^3\frac{m_i^2}{\lambda_i^2}$$

Figures 2a and *b* show the force per unit undeformed area $f=\sigma/\lambda$ in the stretching directions. Following these

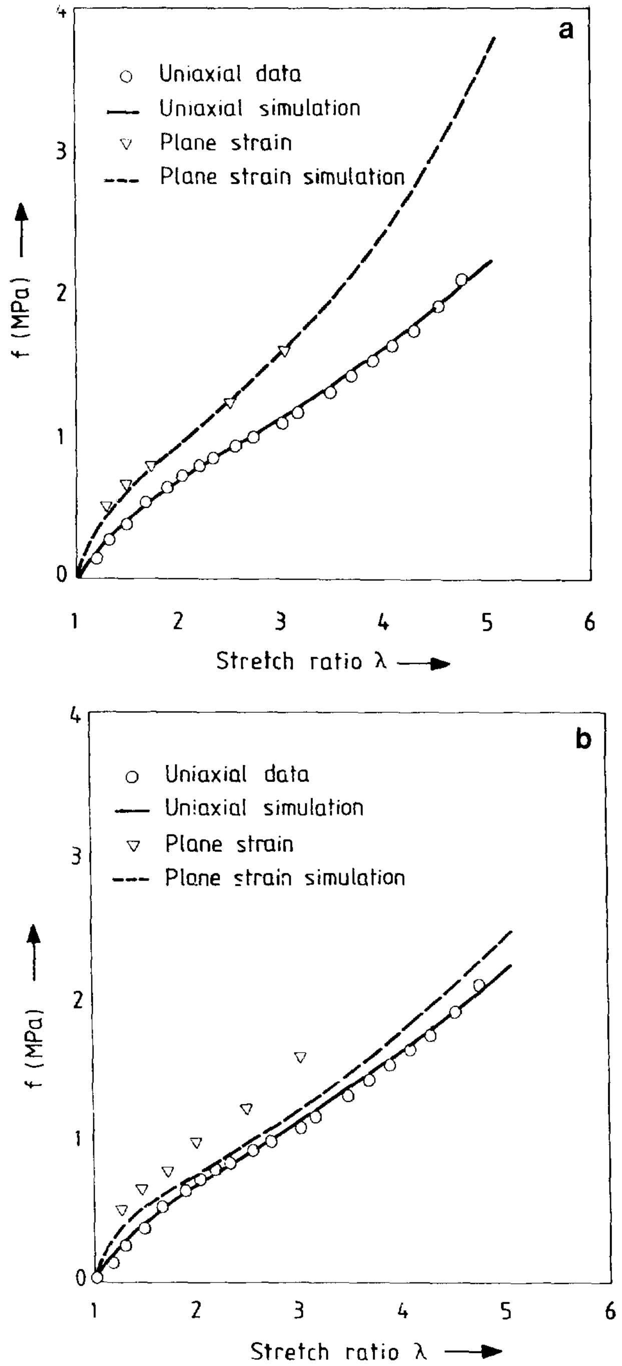

Figure 2 Load *versus* stretch diagram for uniaxial and biaxial tension (or plane strain). The experimental data are taken from James *et al.*[19]. (a) Curves plotted following equation (22) with $C^R=0.4$ MPa, $N=30$. (b) Curves plotted according to the full network model by Wu and Van Der Giessen[8] with $C^R=0.4$ MPa, $N=50$

plots we observe that the proposed model predicts satisfactorily the different behaviour in biaxial extension (or plane strain). The stiffer response of this mode of deformation has been predicted with values of C^R and N fitted in the uniaxial elongation.

Uniaxial and plane-strain compressive deformation

The second set of deformation concerns compression experiments on silicon rubber. Such tests have been investigated by Boyce and Arruda[20] for uniaxial and plane-strain deformations.

In the case of uniaxial compression in the z direction, the deformation tensor is given by:

$$E=\begin{bmatrix} \frac{1}{\sqrt{\lambda}} & 0 & 0 \\ 0 & \frac{1}{\sqrt{\lambda}} & 0 \\ 0 & 0 & \lambda \end{bmatrix} \quad \text{with} \quad \lambda<1 \tag{25}$$

For this mode of deformation the quantities $\alpha(\lambda)$ and $f(\lambda)$ have been calculated analytically by Marrucci[11]:

$$\alpha(\lambda)=\frac{\lambda}{2}\left(1+\frac{\sin^{-1}\sqrt{1-\lambda^3}}{\sqrt{\lambda^3}\sqrt{1-\lambda^3}}\right)$$

$$f(\lambda)=-\frac{\lambda}{4}\frac{1+2\lambda^3}{1-\lambda^3}\left(1+\frac{1-4\lambda^3}{1+2\lambda^3}\frac{\sin^{-1}\sqrt{1-\lambda^3}}{\sqrt{\lambda^3}\sqrt{1-\lambda^3}}\right) \tag{26}$$

Substituting these expressions in equation (22) we obtain the stress in uniaxial compression. In the case of plane-strain compression we use polar coordinates for vector $\boldsymbol{u}$ in the xy plane:

$$u_x=\cos\vartheta, \qquad u_y=\sin\vartheta$$

The deformation gradient tensor E is given by:

$$E=\begin{pmatrix} \frac{1}{\lambda} & 0 \\ 0 & \lambda \end{pmatrix}, \qquad \lambda<1 \tag{27}$$

The quantity $\alpha(E)$ in the plane strain is:

$$\alpha(E)=\alpha(\lambda)=\langle|E\boldsymbol{u}|\rangle_0=\frac{1}{4\pi}\int_0^{\pi}\sqrt{\frac{1}{\lambda^2}\cos^2\vartheta+\lambda^2\sin^2\vartheta}\,\mathrm{d}\vartheta$$

$$=\frac{2}{\pi}\frac{1}{\lambda}\int_0^{\pi/2}\sqrt{1-(1-\lambda^4)\sin^2\vartheta}\,\mathrm{d}\vartheta=\frac{2}{\pi}\frac{1}{\lambda}E(k^2) \tag{28}$$

where $E(k^2)$, the complete elliptical integral of the second kind of modulus $k^2=(1-\lambda^4)$, is given by the series:

$$E(k^2)=\frac{\pi}{2}\left\{1-\frac{1}{2^2}k^2-\frac{1^2 3}{2^2 4^2}k^4-\cdots-\left(\frac{(2n-1)!!}{2^n n!}\right)^2\frac{k^{2n}}{2n-1}\right\} \tag{29}$$

The factor $f(\lambda)$ of equation (22) is given by:

$$f(\lambda)=(Q_{yy}(\lambda)-Q_{xx}(\lambda))\alpha(\lambda)$$

where

$$Q_{xx}(\lambda)=\frac{1}{2\pi\lambda}\int_0^{2\pi}\frac{\cos^2\vartheta}{\sqrt{\cos^2\vartheta+\lambda^4\sin^2\vartheta}}\,\mathrm{d}\vartheta$$

$$=F(k^2)-\frac{1}{k^2}F(k^2)+\frac{1}{k^2}E(k^2) \tag{30}$$

$F(k^2)$ is the complete elliptical integral of the first kind of modulus $k^2=1-\lambda^4$, given by:

$$F(k^2)=\frac{\pi}{2}\left\{1+\left(\frac{1}{2}\right)^2k^2+\left(\frac{1\times 3}{2\times 4}\right)^2k^4+\cdots+\left(\frac{(2n-1)!!}{2^n n!}\right)^2\frac{k^{2n}}{1}\right\}$$

and

$$Q_{yy}(\lambda)=\frac{1}{2\pi}\int_0^{2\pi}\lambda^3\frac{\sin^2\vartheta}{\sqrt{\cos^2\vartheta+\lambda^4\sin^2\vartheta}}\,d\vartheta$$
$$=\frac{1}{2\pi}\lambda^3 4\left[\frac{1}{k^2}F(k^2)-\frac{1}{k^2}E(k^2)\right] \qquad (31)$$

Substituting expressions (28) and (30) in equation (22) we should take into account that the number of segments per unit volume parallel to the xy plane is $2C/3N$, and the component of the contour length in this direction is $\langle L_0\rangle/(2)^{1/2}$; in this case the compressive stress in plane strain deformation is:

$$\sigma=C^{R}\frac{\sqrt{2}}{3}\sqrt{N}\left(\frac{15}{12}\right)^{1/2}L^{-1}\left[\frac{\alpha(\lambda)}{\sqrt{N}}\left(\frac{15}{12}\right)^{1/2}\right]f(\lambda) \qquad (32)$$

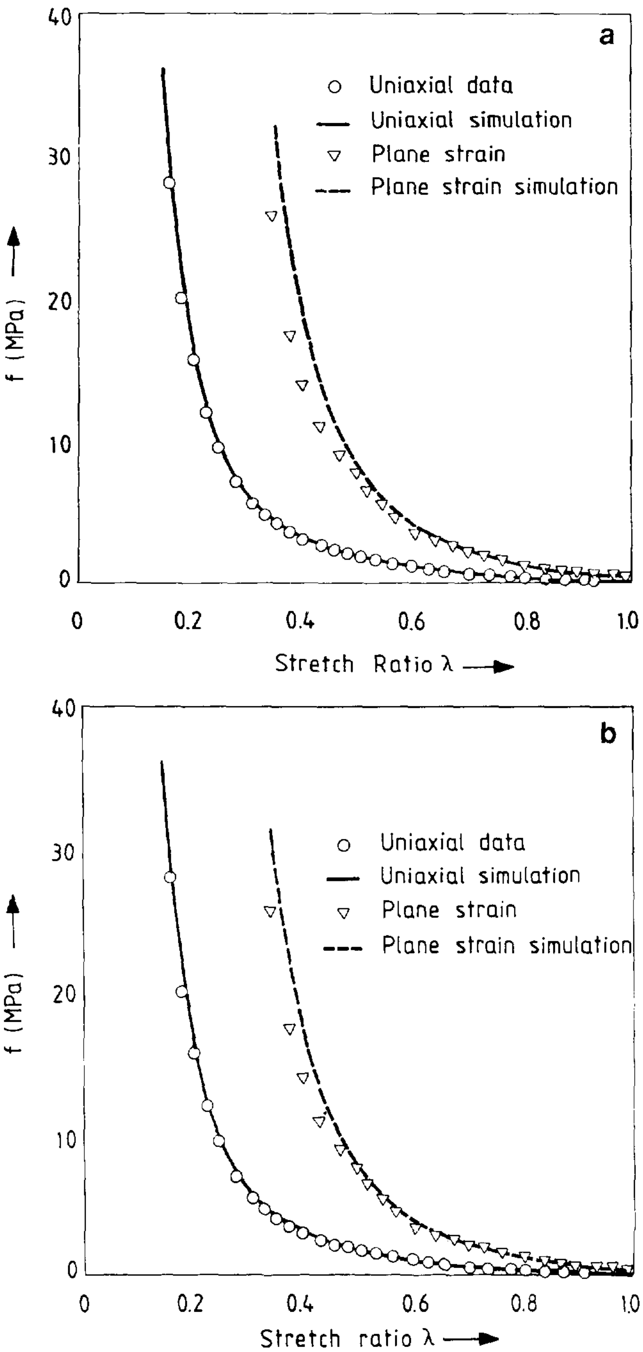

Figure 3 Load *versus* stretch diagram for uniaxial and biaxial compression. The experimental data are taken from Boyce and Arruda[20]. (a) Curves plotted following equation (22) for uniaxial compression and equation (32) for biaxial compression with $C^R=0.435$, $N=8$. (b) Curves plotted according to the full network model by Wu and Van Der Giessen[8] with $C^R=0.435$, $N=7.9$

Figures 3a and *b* show results for uniaxial and plane strain compression for silicon rubber. The values of constants C^R and N used in each model to fit the experimental results are calculated by simulating the uniaxial data. *Figure 3a*, where the results of the above model are plotted, shows a stiffer response in plane strain deformation for $\lambda<0.4$. The same discrepancy is also shown in *Figure 3b* where the full network model[8] is also plotted.

CONCLUSION

The basic formulation introduced by Doi and Edwards, for the description of the primitive chain trapped in a tube-like region, is used in this work for modelling rubber elasticity. Our considerations extended their study for non-Gaussian distribution of the freely jointed segments of a chain. On the other hand, this approach refers to chains which are participating in the rubber network in such a way that relaxation phenomena are not taken into account. The constitutive equation obtained could be applied to large extensions for an arbitrary three-dimensional deformation. Uniaxial and biaxial tensile and compressive experiments with the same network parameters are satisfactorily explained. The capability to capture these tests is compared with the work suggested by Wu and Van Der Giessen, where a full network model accounts for the spatial distribution of the end-to-end vector. The fact that the present model predicts a stiffer response in biaxial stretches, restrains the necessity for a full network description. This is a direct result of the way in which the orientational tensor $Q_{\alpha\beta}(E)$ is calculated. Summation over all possible directions of unit vector $\boldsymbol{u}$ across the primitive chain encloses all possible orientations of network points. On the other hand, at the present state of analysis the role of the mechanically effective entanglements is not treated in a different way from the crosslink points. This implies a constitutive equation which can be applied equivalently in any kind of physical or chemical network junction.

REFERENCES

1 Kuhn, W. *Kolloid Z.* 1934 **68**, 2
2 Kuhn, W. *Kolloid Z.* 1936, **76**, 258
3 Kuhn, W. *Kolloid Z.* 1939, **87**, 3
4 Guth, E. and Mark, H. *Monatsh. Chem.* 1934, **65**, 93
5 Kuhn, W. and Grun, F. *Kolloid Z.* 1942, **101**, 248
6 James, H. M. and Guth, E. *J. Chem. Phys.* 1943, **11**, 455
7 Treloar, L. R. G. and Riding, G. *Proc. R. Soc. Lond. A* 1979, **369**, 261
8 Wu, P. D. and Van Der Giessen, E. *J. Mech. Phys. Solids* 1993, **41**, 427
9 Treloar, L. R. G. *Trans. Faraday Soc.* 1963, **39**, 36
10 Flory, P. J. and Rehner, J. *J. Chem. Phys.* 1943, **11**, 512
11 Marrucci, G. *Rheol. Acta.* 1979, **18**(2), 193
12 Marrucci, G. *Macromolecules* 1981, **14**, 434
13 Edwards, S. F. *Polymer* 1977, **9**, 140
14 Gaylord, R. *Polym. Bull.* 1983, **9**, 181
15 Graessley, W. W. *Adv. Polym. Sci.* 1982, **46**, 67
16 Doi, M. and Edwards, S. F. 'The Theory of Polymer Dynamics', Oxford University Press, New York, 1986
17 Edwards, S. F. *Proc. Phys. Soc.* 1967, **92**, 9
18 Gottlied, M. and Gaylord, R. *Polymer* 1983, **24**, 1644
19 James, A. G., Green, A. and Simson, G. M. *J. Appl. Polym. Sci.* 1975, **19**, 2033
20 Boyce, M. C. and Arruda, E. M. *Polym. Eng. Sci.* 1990, **30**, 1288