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On network descriptions of mechanical and optical properties of rubbers

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ABSTRACT

The non-Gaussian full network model for rubber elasticity is reformulated in a more efficient and more micromechanics-motived manner. Based on such a full network description, a so-called full network model for rubber photoelasticity is proposed, by introducing directional polarizabilities into the individual links of the idealized randomly jointed chain. This optical theory can be used to study the optical properties or birefringence-strain behaviour of rubbers in arbitrary three-dimensional deformation states. Detailed comparisons with two approximate models, namely the classical three-chain model and an eight-chain model for rubber photoelasticity, are provided for different types of deformation. The predicted numerical results are compared with experimental data found in the literature.

§ 1. INTRODUCTION

The present understanding of the mechanical behaviour of amorphous polymers owes much to early advances in the network theory of rubber elasticity (see, for example, Kuhn and Grun (1942) and Treloar (1975)). These theories are based upon the concept of a network of chains of randomly oriented rigid links that are connected at junction points which, in rubber-like materials, are provided by the chemical cross-links between macromolecules. Furthermore, these network theories use a so-called affine deformation scheme, which is based on two key assumptions: (i) statistical fluctuations of the position of the junction points about their mean position can be neglected, (ii) the end-to-end vector of a chain between junction points co-deforms with the local deformation of the continuum it is embedded in. According to this scheme, as deformation progresses each chain stretches while rotating towards a preferred direction. At all stages each chain attempts to maximize its entropy by disorienting the elements or random links, subject only to the constraints imposed by the end-to-end vectors. Another important assumption involved in these network models is that intermolecular interactions are negligible in comparison to intramolecular effects. The overall properties of the network are then obtainable by simply summing the contributions of the individual chains. Furthermore, the exact non-Gaussian treatments of a single chain, both for mechanical and optical behaviour, are available (developed originally by Kuhn and Grun (1942) and James and Guth (1943)). However, exact treatment of the transition from an individual chain to network behaviour is very difficult owing to its mathematical complexity. In principle, this transition (through an averaging process) needs the orientations of the individual chains

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of the network, which was not available for arbitrary three-dimensional (3D) deformations until very recently (Wu and Van der Giessen 1993a).

Various simplified averaging procedures to obtain the network response have been proposed (see Wu and Van der Giessen (1993a)). Among these simplified models, the so-called three-chain model, originally suggested by James and Guth (1943), has become the most widespread and almost standard non-Gaussian network model for rubber elasticity. This model assumes that a network containing *n* chains per unit volume is equivalent to three independent sets of *n*/3 single chains in three orthogonal directions. Thus, the actual spatial distribution of chains is sampled in three orthogonal orientations. Similarly, Treloar (1946) proposed the idea of a four-chain Gaussian network representation (Flory and Rehner 1943) to sample four spatial chain orientations. Very recently, Arruda and Boyce (1991, 1993) proposed a so-called eight-chain model, which considers a set of eight chains connecting the central junction point and each of the eight corners of the unit cube. Obviously, these models are but approximate representations of the actual spatial distribution of molecular chains. All these models can be regarded to sample a set of particular directions among all possible orientations. More precisely, the three-chain model would overestimate the contribution of the chain collection oriented along the direction of major principal extension, while the eight-chain model would underestimate the stiffness of the network because of the excessive freedom of the central junction point in the unit cube (Dahoun, G'Sell, Molinari and Canova 1993). The four-chain model has the major drawback that it does not exhibit the symmetry required of the principal strain space (Arruda and Boyce 1991).

The full network formulation by Wu and Van der Giessen (1992, 1993a) accounts accurately for the actual spatial orientation distribution of molecular chains. Treloar and Riding (1979a) had already developed a rubber elasticity theory based on such a full network description, but their considerations were limited to deformations with biaxial extension along fixed axes under plane stress conditions. Our model extends their theory to a general formulation valid for 3D deformation processes. The modelling centres around a general treatment of the orientation distribution of molecular chains and their evolution as deformation progresses. This description utilizes the idea of a chain orientation distribution function (CODF), which is governed by balance equations that express physically well understood conservation principles. Assuming the network to deform affinely with the deformation of the continuum in which it is embedded, closed-form solutions have been derived for this CODF, which thus contain the complete information of the orientation distribution of molecular chains at any stage of the deformation. This solution is then used to develop the rubber elasticity model by averaging out the contribution to the free energy of individual chains over all chain orientations. The model has been found to be able to pick up the mechanical behaviour of rubbers at various different large deformations (Dahoun 1992, Wu and Van der Giessen 1993a). It has also been successfully used to model the orientation hardening behaviour of large inelastic deformations of amorphous glassy polymers (see, for example, Wu and Van der Giessen (1993a, b, 1994)). G'Sell and Dahoun (1994) and Dahoun *et al.* (1993) used the full network model to describe the amorphous phase responses in their composite model for large plastic deformation of semi-crystalline polymers.

In § 2 of this paper, we reformulate the full network model for rubber elasticity in a more efficient and more micromechanics-motivated manner. The so-derived equations are mathematically equivalent to those given in Wu and Van der Giessen

(1993a). However, the new representation of the model allows us to avoid calculating principal stretches and principal directions of deformations.

The development of molecular chain segment orientation in rubber-like materials under deformation has been extensively studied experimentally, often by the optical anisotropy or birefringence (see, for example, Treloar (1975), Brown and Windle (1984) and Mitchell, Brown and Windle (1985)). In § 3, a so-called non-Gaussian full network model for rubber photoelasticity is proposed. The derivation of this optical theory proceeds along lines parallel to the treatment of the full network model for rubber elasticity. The essential modification is the introduction of directional polarizabilities into the individual links of the idealized randomly-jointed chain. Again, Treloar and Riding (1979b) had already developed a non-Gaussian optical theory based on such a full network description; but, just as for the mechanical properties, their considerations were limited to deformations with biaxial extension along fixed axes under plane stress conditions. Our model extends their theory to a general formulation valid for 3D deformation processes. For the purpose of comparison, we will also give two simplified optical theories corresponding to the so-called three-chain model (see, for example, Wang and Guth (1952)) and eight-chain model (Arruda and Boyce 1993) originally for rubber elasticity (see also Arruda and Przybylo (1993)). The full network model for rubber photoelasticity requires numerical integration; an approximation based on the three-chain and eight-chain representations turns out to be accurate over the entire range of strains. Verification with some experimental results from literature is provided both for the mechanical and for the optical behaviour of a few rubber materials.

Tensors will be denoted by *serif* and vectors by *sans serif* bold-face letters. The tensor product is denoted by $\otimes$ and the following operation for second-order tensors applies ($\mathbf{a} = a_{ij}\mathbf{e}_i \otimes \mathbf{e}_j, \mathbf{b} = b_{ij}\mathbf{e}_i \otimes \mathbf{e}_j, \mathbf{e}_i$ being a Cartesian basis): $\mathbf{ab} = a_{ik}b_{kj}\mathbf{e}_i \otimes \mathbf{e}_j$. Superscripts T and -1 denote the transverse and inverse of a second-order tensor, respectively. The trace is denoted by tr. The three principal values of $\mathbf{a}$ are denoted by $\tilde{a}_i$ where the superposed tilde reminds one of the principal value of the quantity.

§ 2. THE FULL NETWORK MODEL FOR RUBBER ELASTICITY

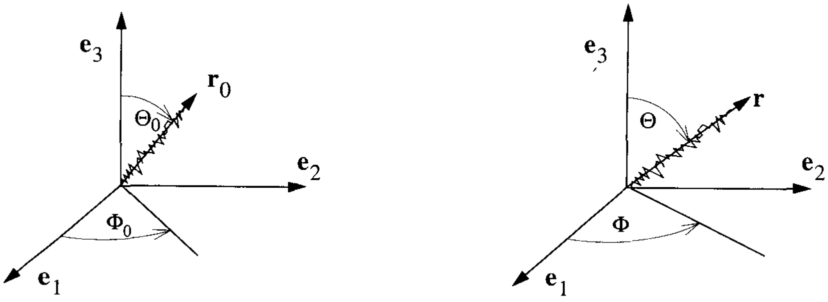
In Wu and Van der Giessen (1993a), we introduced a so-called molecular CODF, denoted by $C(\theta, \varphi; t)$, such that the relative density of molecular chains, at some instant t, whose $\mathbf{r}$-vector orientation falls in the range between (θ, φ) and $(\theta + \mathrm{d}\theta, \varphi + \mathrm{d}\varphi)$, is given by $C(\theta, \varphi; t) \sin\theta \, \mathrm{d}\theta \, \mathrm{d}\varphi$. Note that $\sin\theta \, \mathrm{d}\theta \, \mathrm{d}\varphi$ is the area on a unit sphere spanned by the interval $(\mathrm{d}\theta, \mathrm{d}\varphi)$ and that t is just a time-like parameter. With n denoting the number of chains per unit volume, the actual number of chains between (θ, φ) and $(\theta + \mathrm{d}\theta, \varphi + \mathrm{d}\varphi)$ is then

$$\mathrm{d}n = nC(\theta, \varphi; t) \sin\theta \, \mathrm{d}\theta \, \mathrm{d}\varphi. \qquad (1)$$

For a virgin, unstrained material the orientation of network chains can usually be considered to be disturbed in a random fashion; then C will be independent of θ and φ, and the material's response is instantaneously isotropic. When the material is deformed, all chains are stretched and, at the same time, rotated. Hence, the CODF will develop into a non-uniform distribution which can be quite severe, as has been demonstrated in Wu and Van der Giessen (1993a). Thus, texture development in the sense of molecular chain distributions is described in this model in terms of this CODF.

Assuming the network to deform affinely with some 3D deformation process represented by the deformation gradient tensor $\mathbf{F}$ of the continuum in which it is

Fig. 1



(*a*) (*b*)

A single chain in unstrained (*a*) and strained (*b*) state; definition of geometric quantities.

embedded, each chain's end-to-end vector $\mathbf{r}_0$ in the initial state is taken to be strained and rotated to the vector $\mathbf{r}$ in the current state in an affine manner, i.e. $\mathbf{r} = \mathbf{F}\mathbf{r}_0$. It can be shown (Wu and Van der Giessen 1993a) that in an arbitrary state of deformation, the CODF for an initially random network can be expressed as follows:

$$C = C_0\lambda_c^3(\theta, \varphi; \lambda_i), \tag{2}$$

where $C_0 = 1/4\pi$ is the initial uniform distribution, and where $\lambda_c(\theta, \varphi; \lambda_i)$ is the stretch of an individual chain whose $\mathbf{r}$-vector has an orientation (θ, φ) with respect to the Eulerian triads $\mathbf{e}_i^E$ (i.e. the principal stretch directions in the current configurations), and λ_i are the principal stretches. Here, we have substituted the principal stretches as the time-like parameter t in the previous expressions for the CODF. This is possible since, as a consequence of the affine deformation assumption, the distortion of the network is independent of the rate of deformation, so that t only needs to be some monotonic parameter. Identifying t with λ_i will turn out to be convenient for further development (Wu and Van der Giessen 1993a). For a detailed derivation of eqn. (2) we refer to Wu and Van der Giessen (1993a). It is clear that the Eulerian triads themselves rotate during the deformation process. Therefore, we have to recalculate the principal stretches λ_i and the corresponding principal directions $\mathbf{e}_i^E$ at each stage of the deformation process. Before proceeding it is noted that since we assume the network to be incompressible, the deformation gradient tensor satisfies $\det \mathbf{F} = 1$.

It is noted that the CODF in eqn. (2) is directly related to the stretch of an individual chain and is determined completely through the deformation ellipsoid, which is independent of the coordinate system used. Therefore, we can rewrite eqn. (2) in the form

$$C = C_0\lambda_c^3(\Theta, \Phi; \mathbf{F}), \tag{3}$$

where (Θ, Φ) is the orientation of the $\mathbf{r}$-vector of an individual chain in the current state with respect to a fixed triad $\mathbf{e}_i$ (see fig. 1), and where $\mathbf{F}$ is the deformation gradient tensor. The chain stretch λ_c can be obtained from $\mathbf{F}$ by

$$\lambda_c^{-2} = \mathbf{m}(\mathbf{F}\mathbf{F}^T)^{-1}\mathbf{m}. \tag{4}$$

Here, $\mathbf{m}$ is the unit vector $\mathbf{m} = \mathbf{r}/r = m_i\mathbf{e}_i$ ($r = \|\mathbf{r}\|$) along the end-to-end vector $\mathbf{r}$, in the current deformed state with components

$$m_1 = \sin\Theta\cos\Phi, \quad m_2 = \sin\Theta\sin\Phi, \quad m_3 = \cos\Theta. \tag{5}$$

The actual number of chains between (Θ, Φ) and $(\Theta + \mathrm{d}\Theta, \Phi + \mathrm{d}\Phi)$ is then

$$\mathrm{d}n = nC_0\lambda_c^3(\Theta, \Phi; \mathbf{F}) \sin\Theta \, \mathrm{d}\Theta \, \mathrm{d}\Phi. \tag{6}$$

In order to represent the mechanical properties, let us consider a single chain between two junction points, with its end-to-end vector $\mathbf{r}$ in the current state being specified by angular coordinates Θ and Φ with respect to some fixed frame of reference defined by the set of orthonormal base vectors $\mathbf{e}_i$ (see fig. 1). We further assume that this single chain has a given stretch λ_c in its current state. If the chain contains N links of length l, the length of the unstrained free chain r_0 is given by the root-mean-square value $l\sqrt{N}$. By considering the statistical distribution of possible link angles at a given stretch λ_c, Kuhn and Grun (1942) were the first to derive the well-known non-Gaussian relationship between force f_c and stretch λ_c for the stretched chain in the form

$$f_c = \frac{kT}{l} \mathscr{L}^{-1}\left(\frac{\lambda_c}{\sqrt{N}}\right), \tag{7}$$

where k is Boltzmann's constant, T is the absolute temperature and $\mathscr{L}$ is the Langevin function defined by $\mathscr{L}(\beta) = \coth\beta - 1/\beta$. By noting that $r = \lambda_c r_0 = \lambda_c l\sqrt{N}$, while $1/n$ is the volume per chain and $1/(nr)$ is the cross-sectional area of the chain in the current state, eqn. (7) can be transformed into a relationship between the Cauchy stress σ_c, defined by $\sigma_c = f_c rn$, acting on the continuum in which the chain is embedded and the stretch in the form

$$\sigma_c = C^R\sqrt{N}\lambda_c \mathscr{L}^{-1}\left(\frac{\lambda_c}{\sqrt{N}}\right), \tag{8}$$

where $C^R = nkT$ is known as the rubbery modulus. Now, we can introduce a so-called micro-stress tensor $\boldsymbol{\sigma}_c$ by

$$\boldsymbol{\sigma}_c = \sigma_c(\mathbf{m} \otimes \mathbf{m}) - p\mathbf{I}, \tag{9}$$

which can be interpreted as the contribution of the single chain to the stress of the network. The hydrostatic pressure p is included because of incompressibility. The overall or macro-stress tensor $\boldsymbol{\sigma}$ of the network is then obtained by simply averaging the micro-stress tensor $\boldsymbol{\sigma}_c$ of the individual chains, i.e.

$$\boldsymbol{\sigma} = \frac{1}{n}\int \boldsymbol{\sigma}_c \, \mathrm{d}n. \tag{10}$$

With dn being given by eqn. (6) and the CODF by eqn. (3), we find

$$\boldsymbol{\sigma} = \frac{1}{4\pi}\int_0^{\pi}\int_0^{2\pi} \boldsymbol{\sigma}_c\lambda_c^3 \sin\Theta \, \mathrm{d}\,\Theta \, \mathrm{d}\Phi - p\mathbf{I}, \tag{11}$$

and with eqns. (8) and (9), we finally obtain for the Cartesian stress components, $\boldsymbol{\sigma} = \sigma_{ij}\mathbf{e}_i \otimes \mathbf{e}_j$,

$$\sigma_{ij} = \frac{1}{4\pi} C^R\sqrt{N}\int_0^{\pi}\int_0^{2\pi} \lambda_c^4 \mathscr{L}^{-1}\left(\frac{\lambda_c}{\sqrt{N}}\right) m_i m_j \sin\Theta \, \mathrm{d}\Theta \, \mathrm{d}\Phi - p\delta_{ij}, \tag{12}$$

with λ_c determined from eqn. (4) as a function of the deformation gradient tensor $\mathbf{F}$ and the orientation (Θ, Φ). The hydrostatic pressure p is left unspecified by the constitutive equations and is to be determined from the boundary conditions.

Equations (12) are mathematically equivalent to those given by Wu and Van der Giessen (1993a). However, the new representation of the model allows us to avoid calculating principal stretches and principal stretch directions for arbitrary 3D deformation. Furthermore, this micromechanics-motivated new derivation will turn out to be convenient for further development of the so-called full network model for rubber photoelasticity in the next section.

§ 3. IMPROVED NETWORK MODELS FOR RUBBER PHOTOELASTICITY

It is well-known that many materials show the phenomenon of double refraction, which arises from the fact that they are optically anisotropic. In other words, they have different refractive indices, or polarizabilities in different directions. The refractive index of a material is a function of its response to the electric field in the light wave or, more specifically, of its polarizability, which is defined as the induced dipole moment per unit field strength. Rubber-like materials are usually assumed to be random in their structure and isotropic in the physical properties; such materials do not show double refraction in the initial undeformed state. But in the deformed state, their structures are no longer random; they cease to be isotropic and begin to show double refraction or birefringence.

Usually, developing a network model for rubber photoelasticity follows closely the lines taken in the treatment of the corresponding network model for rubber elasticity. The essential modification is the introduction of directional polarizabilities into the individual links of the idealized randomly-jointed chain. First, the optical properties of the single chain are determined as a function of its length or stretch. Next, the contribution of an individual chain to the polarizability of the network is determined. Finally, the total polarizability of the network is obtained by integration over all the chains.

3.1. *Full network model—Eulerian form*

Consider a single chain at a given stretch λ_c in the current deformed state, with its unit vector $\mathbf{m}$ being specified by angular coordinates Θ and Φ with respect to the base vectors $\mathbf{e}_i$ (see fig. 1). Kuhn and Grun (1942) had shown that a stretched chain can be characterized by polarizabilities γ_1 in the direction of $\mathbf{m}$ and γ_2 in directions $\mathbf{l}$ and $\mathbf{n}$ perpendicular to $\mathbf{m}$. These are given by

$$\gamma_1 = N\left[\alpha_1 - (\alpha_1 - \alpha_2)\frac{2\lambda_c/\sqrt{N}}{\mathscr{L}^{-1}(\lambda_c/\sqrt{N})}\right],$$

$$\gamma_2 = N\left[\alpha_2 + (\alpha_1 - \alpha_2)\frac{\lambda_c/\sqrt{N}}{\mathscr{L}^{-1}(\lambda_c/\sqrt{N})}\right], \tag{13}$$

in terms of the polarizabilities α_1 and α_2 parallel and perpendicular to the link direction respectively. The optical anisotropy or difference of principal polarizabilities may be written as

$$\gamma_1 - \gamma_2 = N(\alpha_1 - \alpha_2)P(\lambda_c), \quad P(\lambda_c) = 1 - \frac{3\lambda_c/\sqrt{N}}{\mathscr{L}^{-1}(\lambda_c/\sqrt{N})}. \tag{14}$$

The contribution of an individual chain to the polarizability of the network can be determined by introducing a so-called chain polarizability tensor $\mathbf{B}_c$ in the form

$$\mathbf{B}_c = \gamma_1\mathbf{m}\otimes\mathbf{m} + \gamma_2\mathbf{n}\otimes\mathbf{n} + \gamma_2\mathbf{l}\otimes\mathbf{l} = (\gamma_1 - \gamma_2)\mathbf{m}\otimes\mathbf{m} + \gamma_2\mathbf{I}. \tag{15}$$

The overall polarizability tensor $\mathbf{B}$ of the network is then readily obtained by simply summing the chain polarizability tensor $\mathbf{B}_c$ of the individual chains, i.e.,

$$\mathbf{B} = \int \mathbf{B}_c \, \mathrm{d}n. \tag{16}$$

With dn given by eqn. (6) and the CODF according to eqn. (3), we obtain

$$\mathbf{B} = \frac{n}{4\pi} \int_0^{\pi} \int_0^{2\pi} \mathbf{B}_c \lambda_c^3 \sin\Theta \, \mathrm{d}\Theta \, \mathrm{d}\Phi. \tag{17}$$

Using eqns. (13) and (15), we find for the Cartesian polarizability tensor components, $\mathbf{B} = B_{ij}\mathbf{e}_i \otimes \mathbf{e}_j$,

$$B_{ij} = \frac{n}{4\pi} \int_0^{\pi} \int_0^{2\pi} \lambda_c^3 (\gamma_1 - \gamma_2) m_i m_j \sin\Theta \, \mathrm{d}\Theta \, \mathrm{d}\Phi + n\gamma_2 \delta_{ij}, \tag{18}$$

with λ_c being given by eqn. (4) and m_i by eqn. (5). The normalized differences of polarizabilities in two orthogonal directions i and j are then given by

$$\beta_{ii} - \beta_{jj} = \frac{B_{ii} - B_{jj}}{n(\alpha_1 - \alpha_2)} = \frac{N}{4\pi} \int_0^{\pi} \int_0^{2\pi} \lambda_c^3 P(\lambda_c)(m_i m_i - m_j m_j) \sin\Theta \, \mathrm{d}\Theta \, \mathrm{d}\Phi, \quad \text{(no sum)}, \tag{19}$$

with $P(\lambda_c)$ being given by eqn. (14).

3.2. *Full network model—Lagrangian form*

The full network model for rubber photoelasticity derived above can also be developed in the initial state, i.e. in a Lagrangian form instead of in the foregoing Eulerian form. The Lagrangian form can be obtained in a rather straightforward manner by employing a direct transformation of eqn. (17). Without going into the details, we give only the result in the form

$$B_{ij} = \frac{n}{4\pi} \int_0^{\pi} \int_0^{2\pi} (\gamma_1 - \gamma_2) F_{ik} F_{jl} m_{0k} m_{0l} \sin\Theta_0 \, \mathrm{d}\Theta_0 \mathrm{d}\Phi_0 + n\gamma_2 \delta_{ij}, \tag{20}$$

with F_{ij} being the Cartesian components of the deformation gradient tensor $\mathbf{F}$. Here, the integrations are performed in the initial orientation state (Θ_0, Φ_0), and $m_{01} = \sin\Theta_0 \cos\Phi_0, m_{02} = \sin\Theta_0 \sin\Phi_0$ and $m_{03} = \cos\Theta_0$ are the components of the unit vector $\mathbf{m}_0 = \mathbf{r}_0/r_0 = m_{0k}\mathbf{e}_k$ along the end-to-end vector $\mathbf{r}_0$ in the initial state (see fig. 1). It is noted that the chain stretch λ_c in eqn. (14) should in this case be determined in the initial state according to $\lambda_c^2 = \mathbf{m}_0(\mathbf{F}^{\mathrm{T}}\mathbf{F})\mathbf{m}_0$.

It is noted that from eqn. (20) we can easily obtain the normalized differences of polarizabilities $\beta_{ii} - \beta_{jj}$ (no sum), which are similar to those given by Treloar and Riding (1979b). However, Treloar and Riding (1979b) limited their attention to two-dimensional (2D) deformations with fixed principal axes of stretching. Our formulation is valid for arbitrary 3D deformations; for the 2D deformations mentioned, the Lagrangian form of our full network model reduces to that in Treloar and Riding (1979b). It is also noted that in the Lagrangian approach, the CODF is not needed at all for the computation of the polarizability tensor of the network. However, the CODF in itself is an essential source of information about the actual orientation distribution of molecular chains at any stage of a general 3D state of deformation (Wu and Van der Giessen 1993a).

3.3. *Simplified models*

In this paper, we shall consider two simplified network models for rubber photoelasticity, namely the three-chain model and eight-chain model. The three-chain model was originally suggested by James and Guth (1943) for rubber elasticity and assumes that a network containing n chains per unit volume is equivalent to three independent sets of n/3 chains per unit volume parallel to the Eulerian principal axes $\mathbf{e}_i^{\mathrm{E}}$. Using the notation $\tilde{B}_i^{3\text{-ch}}$ for the principal network polarizabilities, we thus have

$$\mathbf{B}^{3\text{-ch}} = \sum_{i=1}^{3} \tilde{B}_i^{3\text{-ch}} (\mathbf{e}_i^{\mathrm{E}} \otimes \mathbf{e}_i^{\mathrm{E}}). \tag{21}$$

The normalized differences of the principal network polarizabilities had been given in the form (see, for example, Treloar and Riding 1979b)

$$\frac{\tilde{B}_i^{3\text{-ch}} - \tilde{B}_j^{3\text{-ch}}}{n(\alpha_1 - \alpha_2)} = \tfrac{1}{3}N[P(\lambda_i) - P(\lambda_j)], \tag{22}$$

where λ_i are the principal stretches. The Cartesian components, $\mathbf{B}^{3\text{-ch}} = B_{ij}^{3\text{-ch}} \mathbf{e}_i \otimes \mathbf{e}_j$, can be determined from the principal values $\tilde{B}_i^{3\text{-ch}}$ and principal directions $\mathbf{e}_i^{\mathrm{E}}$ by a standard tensor transformation argument. However, the results cannot be represented by general mathematical formulae for arbitrary 3D deformations.

The eight-chain model for rubber elasticity was proposed by Arruda and Boyce (1991, 1993) and considers a set of eight chains connecting the central junction point and each of eight corners of the unit cube. The polarizability tensor according to the eight-chain model, $\mathbf{B}^{8\text{-ch}}$, is found as

$$\mathbf{B}^{8\text{-ch}} = n \frac{(\gamma_1 - \gamma_2)}{3\lambda_c^2} \mathbf{F}\mathbf{F}^{\mathrm{T}} + n\gamma_2 \mathbf{I}, \tag{23}$$

with

$$\lambda_c = [\tfrac{1}{3}\,\mathrm{tr}\,(\mathbf{F}\mathbf{F}^{\mathrm{T}})]^{1/2}. \tag{24}$$

The tensor $\mathbf{B}^{8\text{-ch}}$ can be represented as $\mathbf{B}^{8\text{-ch}} = B_{ij}^{8\text{-ch}} \mathbf{e}_i \otimes \mathbf{e}_j$. It may be shown that (see also Arruda and Przybylo (1993))

$$\begin{aligned} \beta_{ii}^{8\text{-ch}} - \beta_{jj}^{8\text{-ch}} &= \frac{B_{ii}^{8\text{-ch}} - B_{jj}^{8\text{-ch}}}{n(\alpha_1 - \alpha_2)} \\ &= \frac{N}{3\lambda_c^2} P(\lambda_c)(F_{ik}F_{ik} - F_{jk}F_{jk}), \quad \text{(no sum for } i \text{ and } j\text{)}. \end{aligned} \tag{25}$$

3.4. *Approximation of the full network model*

Comparing the three- and eight-chain samplings with the actual 3D initial random distribution of molecular chains, we expected that, as in the network models for rubber elasticity (Wu and Van der Giessen 1993a), the three-chain model would overestimate the actual optical anisotropy of the network, while the eight-chain model would probably give a lower bound. Indeed, as will be demonstrated in the next section, the optical response predicted by our full network model (18) or (20) is, for the same values of N and n, always in-between that predicted by the three-chain model and eight-chain model, respectively. However, the integrations involved in eqns. (18) and (20) require a rather time-consuming numerical procedure. All these observations motivated us to search for an approximation of the full integration by combining the three-chain and eight-chain models. One possibility is the simple linear combination

$$\mathbf{B} = (1 - \rho)\mathbf{B}^{3\text{-ch}} + \rho\mathbf{B}^{8\text{-ch}}, \tag{26}$$

where the parameter ρ may be a constant or related to some other physical quantity which is, for instance, related to the deformation process. In this paper, we consider ρ to be related to the maximal principal stretch $\lambda_{\max} = \max(\lambda_1, \lambda_2, \lambda_3)$ by

$$\rho = 0{\cdot}62\,\frac{\lambda_{\max}}{\sqrt{N}}, \tag{27}$$

where the factor 0·62 was chosen to give the best correlation will full integrations of eqns. (18) and (20). In this way, the eight-chain contribution in eqn. (23) becomes increasingly important when $\lambda_{\max}$ approaches the limit stretch $\sqrt{N}$. The form of eqn. (26) is similar to our previous proposition for the full network stress in rubber elasticity in relation to that according to three- and eight-chain models (Wu and Van der Giessen 1993a).

3.5. *Calculation of birefringences*

In an optical anisotropic medium the properties are represented by the refractive index ellipsoid, the principal axes of which represent the three principal indices $\tilde{\mu}_i$ in three mutually perpendicular directions. This in turn is related to the polarizability ellipsoid, whose axes correspond to the principal polarizabilities $\tilde{B}_i$, and coincide in direction with the axes of the refractive index ellipsoid. The conversion of polarizabilities $\tilde{B}_i$ (per unit volume) to refractive indices $\tilde{\mu}_i$ makes use of the Lorentz–Lorenz relation

$$\frac{\tilde{\mu}_i^2 - 1}{\tilde{\mu}_i^2 + 2} = \frac{4\pi}{3}\tilde{B}_i. \tag{28}$$

Since the differences of refractive index relative to the mean value μ_0 are generally small, it may be shown that

$$\frac{\tilde{\mu}_i^2 - 1}{\tilde{\mu}_i^2 + 2} \approx \left[\frac{\tilde{\mu}_0^2 - 1}{\tilde{\mu}_0^2 + 2} - \frac{6\mu_0^2}{(\mu_0^2 + 2)^2}\right] + \frac{6\mu_0}{(\mu_0^2 + 2)^2}\tilde{\mu}_i,$$

so that

$$\tilde{\mu}_i = \Delta\mu_0\tilde{B}_i - M_0, \tag{29}$$

with

$$\Delta\mu_0 = \frac{4\pi}{3}\frac{(\mu_0^2 + 2)^2}{6\mu_0}, \quad M_0 = \frac{(\mu_0^2 - 1)(\mu_0^2 + 2) - 6\mu_0^2}{(\mu_0^2 + 2)^2}.$$

Applying the relationship (29) for all three principal directions, we find that the polarizability tensor $\mathbf{B}$ and the refractive index tensor $\boldsymbol{\mu}$, formed from the principal values $\tilde{\mu}_i$, are related through

$$\boldsymbol{\mu} = \Delta\mu_0\mathbf{B} - M_0\mathbf{I}. \tag{30}$$

Since the polarizability ellipsoid is coaxial with the refractive index ellipsoid, the birefringence for propagation of light along any direction is determined by the polarizabilities in the two transverse directions (directions of electric vector). Therefore, for instance, propagation along $\mathbf{e}_3$ involves the difference of polarizabilities $B_{11} - B_{22}$.

Using eqn. (30), we obtain equations in the form

$$\mu_{ii} - \mu_{jj} = \frac{4\pi}{3} \frac{(\mu_0^2 + 2)^2}{6\mu_0} (B_{ii} - B_{jj}), \quad \text{(no sum)}, \tag{31}$$

or

$$\mu_{ii} - \mu_{jj} = \Delta\mu_N(\beta_{ii} - \beta_{jj}), \quad \text{(no sum)}, \tag{32}$$

with

$$\Delta\mu_N = \frac{4\pi}{3} \frac{(\mu_0^2 + 2)^2}{6\mu_0} n(\alpha_1 - \alpha_2).$$

Here, μ_{ij} are the components of the refractive index tensor $\boldsymbol{\mu}$ defined by $\boldsymbol{\mu} = \mu_{ij}\mathbf{e}_i \otimes \mathbf{e}_j$.

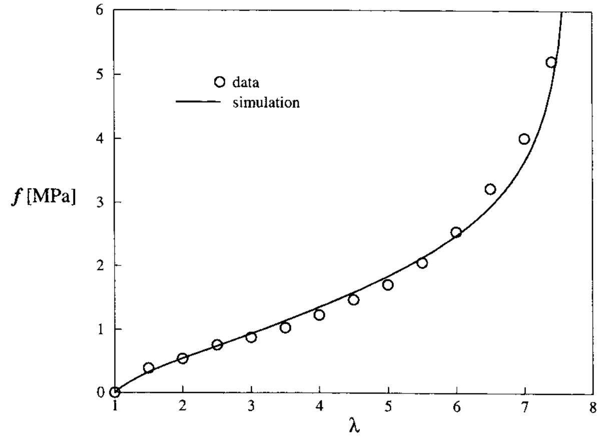
§ 4. RESULTS

The full network model for rubber elasticity has been used to describe the large-strain elastic behaviour of rubber-like materials (Wu and Van der Giessen 1993a). Detailed comparisons with experimental results and with two approximate models have been provided for different types of deformation and rubbers (Wu and Van der Giessen 1993a). As an additional example of the application of the model, we study the mechanical responses to uniaxial tension and pure shear of a vulcanized rubber reported by Treloar (1944) but, according to the new derivation of the full network model given in § 2. This also serves as a numerical check on the present network formulation compared to the previous one (Wu and Van der Giessen 1993a). At each stage of the deformation, the double integral in the full network relation (10) is evaluated by first noting that due to symmetry only the intervals $\Theta \in [0, \pi/2], \Phi \in [0, \pi]$ need to be considered, then subdividing that area into a number of cells and integrating within each cell using Gaussian quadrature. Recursive refinement is applied for each cell until the integral is obtained with a relative error of 10^{-5}.

As pointed out by Wu and Van der Giessen (1993a), the full network model as well as the simplified three-chain model and eight-chain model are able to reproduce experimental rubber stress–strain data for a certain deformation and material by selecting the material parameters N and C^R for the given model. However, a more important aspect appears to be the description of the network response under different states of deformation. In order to assess the deformation dependence, we take the following procedure (see also Arruda and Boyce (1993), Wu and Van der Giessen (1993a)). The network parameters N and C^R are fitted from uniaxial tension data, and are then used to predict pure shear. Figure 2 shows results for uniaxial tension in terms of the nominal stress f or load per unit undeformed area as a function of the uniaxial stretch λ. The values of $N = 62$ and $C^R = 0{\cdot}3$ MPa were found to give the best correlation with the uniaxial tension data (Treloar 1944). The predicted results of pure shear using these values of the parameters are given in fig. 3. The pure shear is characterized by the principal stretches $\lambda_1 = \lambda, \lambda_2 = 1, \lambda_3 = 1/\lambda$ along fixed directions, while the material is in a state of plane stress, i.e. $\sigma_{33} = 0$. The figure shows the load in the stretching direction, i.e. $f = \sigma_{11}/\lambda$. It is observed that the full network model predicts the different behaviour in pure shear well over the entire experimental range.

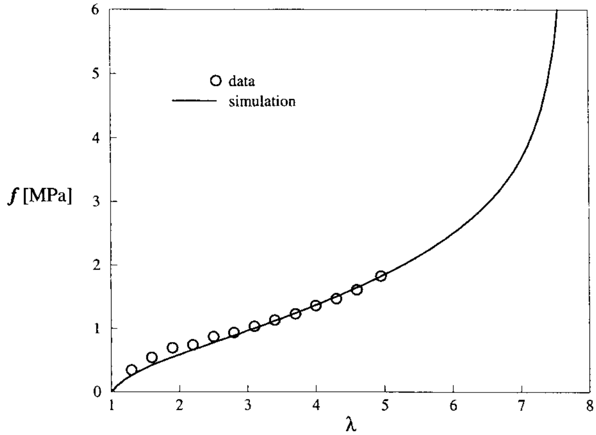
We proceed by studying the optical properties of rubbers in terms of the full network model as well as the simplified three-chain and eight-chain models for rubber photoelasticity. The numerical procedure of the integrations (18) and (20) involved in the full network model is similar to that in the mechanical description (12) of the full network given above. However, the integrals in eqns. (18) and (20) are 'well behaved' over the whole of the specified ranges (Treloar and Riding 1979b). This is due to the

Fig. 2



Load against stretch diagram for uniaxial tension of a vulcanized rubber according to the full network model for rubber elasticity with $N = 62$ and $C^R = 0{\cdot}3$ MPa. The experimental data are taken from Treloar (1944).

Fig. 3

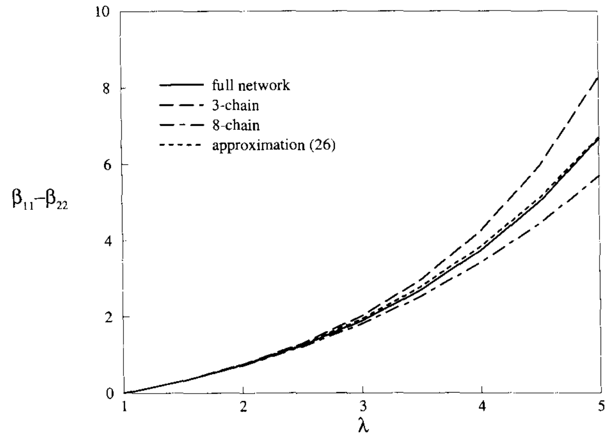


Load against stretch diagram for pure shear of a vulcanized rubber according to the full network model for rubber elasticity with $N = 62$ and $C^R = 0{\cdot}3$ MPa. The experimental data are taken from Treloar (1944).

fact that whereas the tensile stress σ_c on the single chain tends to infinity as its stretch λ_c approaches the limit stretch N (see eqn. (8)), the optical anisotropy of the chain remains finite and reaches the value $n(\alpha_1 - \alpha_2)$ (see eqns. (14)). As a result, the amount of computation required to achieve any degree of accuracy is notably less for the optical than for the mechanical problem.

Figure 4 shows the predicted difference in polarizability for uniaxial tension in the $\mathbf{e}_1$ direction with principal stretches $\lambda_1 = \lambda, \lambda_2 = \lambda_3 = \lambda^{-2}$. The value $N = 25$ was used for all three models; it was simply used as a representative value of N. What this result clearly shows is that relative to the full network model for rubber photoelasticity, the simplified three-chain model tends to overestimate the optical anisotropy at large stretches, while the eight-chain approximation tends to underestimate it. It is also

Fig. 4



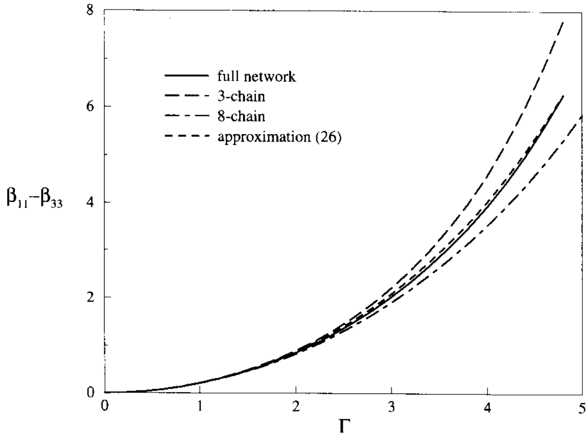
Predicted normalized optical anisotropy against stretch diagram for uniaxial tension according to different network models for rubber photoelasticity with $N=25$.

observed that all models give virtually identical predictions for small stretches up to $\lambda \approx 2{\cdot}5$ (or roughly 50% of the limit stretch). The difference at large stretches seems to be associated with the different limit stretches of the complete network. The stretching according to the three-chain model is limited directly by the tensile stretch $\lambda_L = \sqrt{N}$ of the chains parallel to the tensile direction, while the overall network limiting stretch for the eight-chain model exceeds λ_L. It is seen that the approximation (26) for the full network optical response is indeed very accurate up to very large stretches.

Next, we consider the case of simple (and *not* pure) shear, where the deformation gradient tensor $\mathbf{F}$ is given by $\mathbf{F} = \mathbf{I} + \Gamma \mathbf{e}_1 \otimes \mathbf{e}_2$. In contrast to uniaxial tension where the principal stretch directions are fixed in space, the principal stretch directions in simple shear rotate constantly during the deformation process. As a result, the prediction of the optical anisotropy in simple shear is much more involved than in the deformations with fixed principal stretch directions. Figure 5 shows the predicted optical anisotropy of simple shear according to the full network model, three-chain and eight-chain network models for rubber photoelasticity. The differences in predicted normalized optical anisotropy $\beta_{11} - \beta_{33}$ between the network models are similar to those presented in fig. 4 for uniaxial tension. Compared with the CODF in simple shear presented in Wu and Van der Giessen (1993a), it is found that all models support the observation that molecular chains rotate towards the shear direction. Again, the approximation (26) for the full network optical response in terms of $\beta_{11} - \beta_{33}$ is very accurate up to very large shear strains.

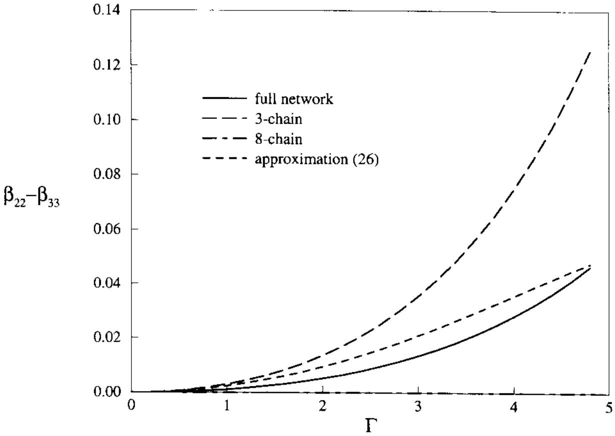
It is well-known that the secondary normal stresses σ_{11} and σ_{22} during simple shear are mainly due to the development and subsequent rotation of the induced anisotropy, and that the prediction of these mechanical phenomena generally shows a rather strong dependence on the constitutive models (see, for example, Wu and Van der Giessen (1993a, 1994)). It is expected that the secondary order effects in optical anisotropies such as $\beta_{22} - \beta_{33}$ will also depend strongly on the constitutive models for rubber photoelasticity. Figure 6 shows the predicted secondary optical anisotropy $\beta_{22} - \beta_{33}$ during simple shear. Although the predicted absolute values of $\beta_{22} - \beta_{33}$ are much smaller than those of $\beta_{11} - \beta_{33}$, the relative differences in predicted $\beta_{22} - \beta_{33}$ between the network models are much larger than those in predicted $\beta_{11} - \beta_{33}$. In fact, according

Fig. 5



Predicted normalized optical anisotropy β_{11}–β_{33} against shear strain diagram during simple shear according to different network models for rubber photoelasticity with $N = 25$.

Fig. 6

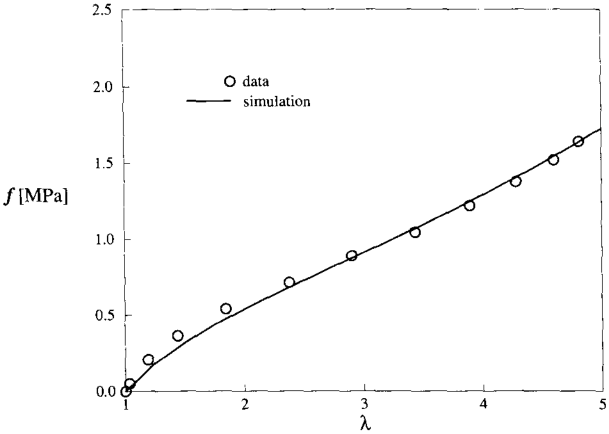


Development of secondary optical anisotropy β_{22}–β_{33} during simple shear according to different network models for rubber photoelasticity with $N = 25$.

to the eight-chain model, $\beta_{22} - \beta_{33} \equiv 0$ during simple shear (see eqns. (25)). This fact is also the reason why the approximation (26) for the full network optical response in terms of $\beta_{22} - \beta_{33}$ is not very good in this special case.

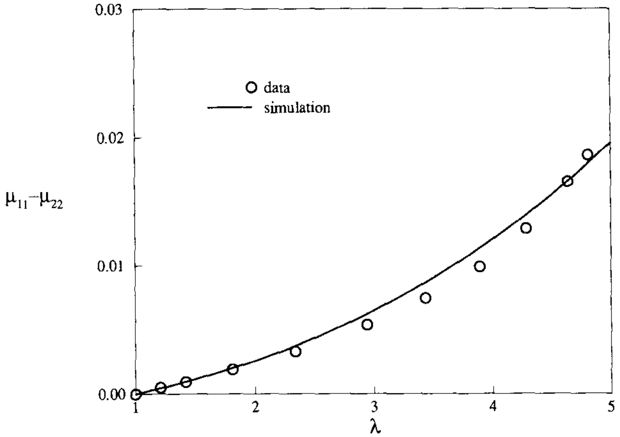
Doherty, Lett and Treloar (1980) made simultaneous measurements of stress and birefringence for a vulcanized styrene-butadiene rubber (SBR) under uniaxial tension. The values of $N = 75$ and $C^{R} = 0{\cdot}3$ MPa according to our full network model for rubber elasticity are determined; the fit is shown in fig. 7. The so-determined value of $N = 75$ is then used to predict birefringence according to our full network model for rubber photoelasticity. For that purpose, a value for the intrinsic birefringence $\Delta\mu_N$ must be estimated for a quantitative prediction. The simulated birefringence-stretch curve is presented in fig. 8, where a value for the intrinsic birefringence $\Delta\mu_N = 3{\cdot}6 \times 10^{-3}$ was chosen to give the best correlation with the experimental data. The value of $\Delta\mu_N$ seems to be reasonable (see, for example, Treloar (1975)). It is observed that the full network

Fig. 7



Load response to uniaxial tension of a vulcanized styrene-butadiene rubber (SBR) according to the full network model for rubber elasticity with $N = 75$ and $C^R = 0{\cdot}3$ MPa. The experimental data are taken from Doherty *et al.* (1980).

Fig. 8



Predicted birefringence in uniaxial tension of a vulcanized styrene-butadiene rubber (SBR) according to the full network for rubber photoelasticity with $N = 75$ and $\Delta\mu_N = 3{\cdot}6 \times 10^{-3}$. The experimental data are taken from Doherty *et al.* (1980).

model for rubber photoelasticity is able to capture the optical behaviour, at least qualitatively.

§ 5. DISCUSSION AND CONCLUSIONS

In this paper, the full network model for rubber elasticity has been reformulated in a more efficient and more micromechanics motivated manner. The equations are mathematically equivalent to those given in Wu and Van der Giessen (1993a). However, the new representation of the model allows us to avoid calculating principal stretches and principal stretch directions of deformations. The predicted numerical results have been compared with experimental data for a vulcanized rubber under uniaxial tension and pure shear. The comparison further supports our conclusion (Wu and van der

Giessen 1993a): the full network model for rubber elasticity does pick up the dependence of the state of deformation observed experimentally in rubber materials.

We have developed a so-called full network model for rubber photoelasticity. The derivation of this optical theory follows similar lines as the treatment of the full network model for rubber elasticity. The essential modification is the introduction of directional polarizabilities into the individual links of the idealized randomly joined chain. Our full network optical theory has extended Treloar and Riding's (1979b) analysis for biaxial extension with fixed principal stretch directions to general 3D deformation processes. We have also presented a so-called eight-chain network optical theory, which is equivalent to that discussed by Arruda and Przybylo (1993), and have considered the classical three-chain network optical theory. The three-chain model and eight-chain model are both based on approximate descriptions of an affine network model, while our full network theory is based on an exact treatment of that same concept. The purpose of studying the full network model for rubber photoelasticity here in some detail is to assess the accuracy of the three-chain and eight-chain model. The general tendency of the predictions of these simplified models compared with the more exact full network theory is that with the same network parameters, the three-chain model overestimates the optical anisotropy of the network at large strains, while the eight-chain model underestimates the optical anisotropy. At small strains the models are indistinguishable.

In general, the form of the relations between polarizabilities and applied strains is very similar to that for the corresponding stresses. However, the specific non-Gaussian features are quantitatively less pronounced. This is due to the fact that whereas the tensile stress σ_c on a single chain tends to infinity as its stretch λ_c approaches the limit stretch $\sqrt{N}$, the polarizability of the chain remains finite throughout. It is noted that the relative differences between various network models in predicted optical properties are smaller than in predicted mechanical properties at large strains, using the same value of N. Furthermore, the factor 0·62 was used in the approximation of the full network model in the description of optical properties (see eqns. (26) and (27)), while the factor 0·85 in the description of mechanical properties gave the best correlation with the full network model (Wu and Van der Giessen 1993a). From a numerical point of view this also has to be attributed, to some extent, to the fact that the specific non-Gaussian features are quantitatively less pronounced in the optical behaviour of rubbers.

The predicted numerical results according to the full network optical theory have been compared with experimental data for a vulcanized styrene-butadiene rubber under uniaxial tension. Although a value for the intrinsic birefringence $\Delta\mu_N$ was estimated, the full network optical theory was found to be able to capture the optical behaviour of rubbers, at least qualitatively. A quantitative comparison needs more experimental data for different types of deformation and materials. However, experiments for optical properties are much less available than for mechanical properties of rubbers. Furthermore, theoretical and experimental studies on optical properties presented in the literature have been limited to one-dimensional or 2D deformations with fixed principal stretch directions in space, as far as the authors are aware. Analysis of optical anisotropy in deformations, including arbitrary rotations of the principal strain axes, is of theoretical and practical importance. Obviously, large simple shear is a typical large-strain and large-rotation problem. The present study of optical anisotropies under simple shear has shown that the full network, as well as the three-chain network and eight-chain network optical theories, correctly predict that the molecular chains rotate continuously towards the shear direction. A more important aspect seems to be that the prediction of the secondary optical anisotropy $\beta_{22} - \beta_{33}$ during simple shear is strongly dependent on the constitutive models. Thus, the simple shear test seems to provide a simple yet effective means for assessing the adequacy of non-Gaussian network models for rubber photoelasticity.

Finally, it is well-known that if the number of links N is large, the orientation distribution of the individual links with respect to the end-to-end vector has been given by Kuhn and Grun (1942) analytically. Furthermore, a closed-form solution for the molecular CODF has been derived by Wu and Van der Giessen (1993a). Therefore, it is possible to obtain analytically a so-called link orientation distribution function, which would be expected to contain the complete information of the orientation distribution of molecular links at any stage of the deformation.

This paper is mainly concerned with the formulation of network optical theories and their constitutive differences. Further refinement of the models and detailed comparisons with experimental data are in progress and will be reported elsewhere.

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