Mechanical behaviour of PVC: model evaluation

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MECHANICAL BEHAVIOUR OF PVC: MODEL EVALUATION

BY
DMYTRO MIROSHNYCHENKO

A MASTER'S THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF MASTER OF PHILOSOPHY OF LOUGHBOROUGH UNIVERSITY DECEMBER 2001

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Table of Contents

Introduction

1 The Arruda and Boyce model and its evaluation
1.1 Introduction ................................................. 6
1.2 On the strain-energy function .......................... 7
1.3 The Arruda and Boyce eight-chain model .............. 8
1.4 The experimental data due to Treloar .................. 9
1.5 Comparison with the first stretch invariant model .... 13
1.6 Modification of the strain energy into the additive form 18

2 The Turner and Brennan composite model and its evaluation
2.1 Introduction .................................................. 30
2.2 The Poisson ratio approach .............................. 31
2.3 The experimental data due to Kawabata ................. 32
2.4 The filament theory and the composite model ......... 35
2.5 Prediction of the stress in uniaxial and equibiaxial extensions .... 42
2.6 Model evaluation in non-equibiaxial extension ....... 45
2.7 On the standard deviations in the prediction of the Treloar data 52

3 The yield stress of oriented PVC and its prediction
3.1 Introduction ................................................ 66
3.2 The filament model for the yield stress of oriented material 67
3.3 The experimental data on the yield stress of oriented PVC 69
3.4 Prediction of the yield stress of oriented PVC ........ 73

Bibliography ............................... iv
Abstract

The work compares the capability of three simple models to reproduce the nonlinear elastic behaviour of rubberlike materials using experimental data due to Treloar and to Kawabata. These are the Arruda and Boyce eight-chain model, the first stretch invariant model, and the Turner and Brennan composite model.

The eight-chain model produces very similar results to those of the first stretch invariant model, and thus it is shown that it can not be much improved within these limitations.

The composite model gives excellent agreement with the extensive data due to Kawabata and it conforms much more closely to the quintessential data due to Treloar than the two other models in focus.

Then the composite model is applied to predict the yield stress of oriented PVC. Thereto a set of experiments has been performed to determine the variation of the yield stress with orientations for different pre-stretches. The agreement between the prediction and the experimental results is proven to be quite satisfactory.
Acknowledgements

I would like to thank Tony Green and Marianne Gilbert, my supervisors, for their many suggestions and constant support and understanding during this research. I am also thankful to Dave Hitt and Ray Owens for their guidance through my experimental work in IPTME.

I had the pleasure of meeting Duncan Wormald and Les Holloway, the representatives of Wavin Industrial Products Ltd, and Tony Day from Hydro Polymers Ltd. They are friendly people and their support makes this research possible.

I am also grateful to Leno Mascia for allowing me to attend his course on polymer properties (mechanics of polymers), which provided me a better insight into viscoelasticity.

Finally, I would like to acknowledge my gratitude to people from the Department of Mathematical Sciences and to my friends from other departments of Loughborough University for their help and support.

Loughborough, Leicestershire, UK
5 October 2001

Dima Miroshnychenko
Introduction

The present study involves modelling the mechanical behaviour of rigid PVC material. Herein we endeavour to evaluate the capability of different mathematical models to predict nonlinear elastic properties of drawn PVC samples in order to extend boundaries of our understanding for further development.

Resulting from previous research undertaken in IPTME at Loughborough University considerable experimental data [9–13, 15, 19, 25] have already been accumulated on the nonlinear mechanical response of PVC material to deformation, and these together with data due to Treloar [20], considered by many to be the quintessential rubber data, and data due to Kawabata [14], who performed extensively not only uniaxial and equibiaxial tests but also non-equibiaxial ones, provide a starting point in our analysis. As our modelling proceeds incorporating further tensile properties (in particular, yield) of PVC material, it would be necessary to design new experiments to provide specific data for model evaluation.

Our particular interest lies in mathematical modelling the mechanical behaviour of PVC at room temperature following a prescribed planar deformation carried out above a glass transition temperature (at which a polymer undergoes the glass to rubber transition), that corresponds to a discontinuity of physical parameters (and in particular of the thermal expansion coefficient). In this prescribed deformation the material is allowed to cool under restraint, giving rise to an oriented product with enhanced mechanical properties such as increased yield stress and failure strength.
The enhanced properties in one direction are accompanied by lowering the properties in the other.

Orientation is being used increasingly to enhance product properties. Examples for PVC include stretch blow moulded bottles, corrugated roofing sheet and pipe, as well as film products and flexible shrink sleeving. The growing importance and commercialisation of oriented products has recently been highlighted [26–28].

The enhanced mechanical properties which are to be modelled arise through the process of deforming the material at a temperature above its glass transition temperature, $T_g$, and then allowing it to cool to room temperature whilst still under load. If unloading is allowed to take place at the drawing temperature the result is a virtually complete recovery of the deformation. Unloading at room temperature gives rise to enhanced properties including increased yield and tensile strength (with an accompanying reduction in strain to failure), as well as increased impact strength. For uniaxially or unequal biaxially oriented samples, property anisotropy is observed.

The deformation behaviour of PVC is controlled by its physical structure, which is unusual, since it is neither a conventional crystalline polymer, containing spherulites, nor a totally amorphous one. It contains about 10% crystallinity, which is present as small crystallites approximately 10 nm in diameter joined together by a myriad of long chain molecules whose lengths considerably exceed the mean distance between crystallites. The structure thus has a form similar to that of crumpled chicken wire with the crystallites at the nodes, but with a large number of crumpled strands joining the nodes. When the material is deformed by the action of external forces above $T_g$, the performance is that of a network. The initially crumpled long chains are progressively straightened and the crystallites rotate so that the structure takes up some preferred orientation [8].

Rigid PVC has a $T_g$ of about 80°C, so that any orientation produced at higher
temperatures is "frozen in" on cooling below this temperature. The maximum extensibility of rigid PVC is achieved at about 90°C, an effect attributable to the network structure described above [12].

The tensile properties in focus are the deformation and yielding at room temperature of rigid PVC sheets which have been stretched at temperatures $\geq 90^\circ$C and then allowed to cool to room temperature whilst being held in the stretched state. The work of other investigators would indicate that the effect of the hot working is to introduce a residual stress state into the material. Put crudely, this is based on a two mechanism model in which it is assumed that the chains stretch elastically but that there is a viscoelastic resistance to the relative motion of the chains. With the stretched material held at high temperature, the viscoelastic stresses relax leaving the elastic chain stresses which on unloading would tend to make the material recover to its original length. However, since the unloading is at much lower temperature, below $T_g$, the viscoelastic modulus is much higher and this opposes the recovery so that the sheet remains in its stretched state. It is therefore assumed that before the material can yield it is first necessary to counteract the residual stress and that additional stresses over and above this value will be required in order to produce yielding.

Experimental evidence [15] accumulated previously shows that for unoriented samples yield generally occurs through the local formation of a neck, followed by the growth of the necked region until the entire gauge length of the test specimen has undergone the necking. This stage is followed by a short stage of uniform extension prior to fracture. The amount of necking depends strongly on the prior hot deformation of the material and for sufficiently large prior deformation no necking takes place and the deformation is a uniform extension followed by fracture.

The aim of our evaluation is to utilise such a mathematical model, which would be consistent with the structure described, would replicate the various processes undergone by the polymer, and which constitutive equations, being simple and tangible,
would correctly predict the stresses required to bring about further (possibly non-uniform) deformation of the material.

Much of the published work on biaxial deformation of polymers is concerned with the modelling of deformation processes; our interest lies in modelling the subsequent properties of the stretched polymer. Related work is being carried out at a number of institutions. Buckley and co-workers [4, 5, 7] have developed a system of constitutive equations in differential form, which model the mechanical behaviour of amorphous polyethylene terephthalate at temperatures near its $T_g$. Sweeney and Ward [17, 18] have modelled the multiaxial stretching of PVC both immediately below and immediately above its glass transition temperature. Other relevant work is that due to Arruda and Boyce and co-workers [1–3] who have derived constitutive equations governing the plastic deformation of a range of glassy polymers. The mechanics of neck formation and growth in the cold drawing of elastic films has been studied by Coleman and Newman [6] for isotropic materials.

It is proposed to base the model for determining the residual stress on an approach similar to that used by Turner and Brennan [23, 24] and by Arruda and Boyce [1]. Both assume that the elastic energy due to the chain stretching is a function of the first invariant of the stretch tensor and from this it is possible to get expressions for the stresses. A more general approach would be to assume that the strain energy depends on the first and second invariants of the stretch tensor and it might be necessary to adopt this model in the light of the experimental results.

Therefore in general it is necessary to carry out a series of tests in which the stress history during the hot stretching process would be monitored as a function of the stretching mode and draw ratios in order to determine the form of the strain-energy function. Unfortunately, at the time the research was being conducted the equipment had not been ready for this kind of experiments, and therefore in particular we based our study on the data due to Treloar and extensive data due to Kawabata on the
rubber material.

To predict the yield stress of oriented PVC material it is necessary to take into account the material anisotropy resulting from the pre-stretching, and it is proposed to incorporate this in the model by residual stresses as well.

In order to examine the proposed model for yielding deformation it is necessary to produce sheets with different draw ratios and carry out a series of uniaxial tensile tests on specimens cut at a range of orientations relative to the principal stretch directions of the sheet.

The establishment of a model governing the mechanical behaviour of oriented PVC material will provide the stress analyst with a series of equations from which the subsequent deformation and flow under a variety of loading conditions can be predicted. The ability to perform these predictions can in turn lead to the identification of design criteria for the industrial application of these oriented materials. Models produced would be of particular interest to product designers, and plastics processors involved in the development of oriented processes and polymer suppliers.
Chapter 1

The Arruda and Boyce model and its evaluation

In this chapter we explore how the stress-strain relations are determined through the strain energy. Then we evaluate the predictive capability of the Arruda and Boyce eight-chain model to reproduce the experimental results by Treloar in juxtaposition with the first stretch invariant model. The comparison has revealed that Arruda and Boyce indeed achieved quite a remarkable approximation to the strain-energy function dependent on the first invariant of stretch tensor only. In the attempt to modify the eight-chain model and to predict more accurately the mechanical behaviour of rubberlike materials we also consider a more general type of the strain energy, consequently reducing it to the simple additive form of two functions dependent on first and second invariants of the stretch tensor correspondingly. Quite a simple and plausible assumption about a linear relation between the first stretch invariant function of the newly amended model and the strain-energy function derived for the eight-chain model reduces the former model to nothing else but the Arruda and Boyce model itself. In Chapter 2 we extend our evaluation onto the Turner and Brennan composite model.
1.1 Introduction

One of the models in focus is that due to Arruda and Boyce [1] who have derived constitutive equations governing the elastic deformation of rubberlike materials that possess the underlying macromolecular network structure which exhibits the non-Gaussian behaviour of its individual chains. The developed constitutive relation is based on an eight-chain representation which accurately captures the cooperative nature of network deformation. The model involves a strain-energy function, that is dependent on the first invariant of the stretch tensor only, and requires only two material parameters, an elastic modulus and a limiting chain extensibility.

The results of their eight-chain model as well as those of several prominent models were [1] compared with experimental data due to Treloar [20]. Arruda and Boyce [1] illustrated the simplicity and effectiveness of their model over the earlier models.

Herein we put this eight-chain model [1] to the test, juxtaposing it with the arbitrary first stretch invariant model. Particularly, we exploit the experimental data due to Treloar for the uniaxial extension to predict on the basis of the first stretch invariant model the results in equibiaxial extension. Then we compare those values of the stress predicted with the results of the Arruda and Boyce model in equibiaxial extension.

In the last section, we consider a more general type of the strain energy. Reducing it to the simple additive form of two functions dependent on first and second invariants of the stretch tensor correspondingly, we attempt to modify the Arruda and Boyce model in order to improve the accuracy. Therein we employ quite a simple and plausible assumption about a linear relation between the first stretch invariant function of the newly amended model and the strain-energy function derived by Arruda and Boyce in their paper [1].
1.2 On the strain-energy function

This section introduces some preliminaries about the determination of the stress-strain relations through the strain energy, and this gives a fairly general insight into the basis of the Arruda and Boyce treatment in general and the derivation of the strain-energy function for their eight-chain model in particular, which are discussed in the next section.

The stress-strain relation is automatically determined once a function for the strain energy is chosen. Its choice is generally unrestricted but not completely. In this section we also point out some certain requirements of logical consistency which determine at least some properties of strain-energy function.

The interrelationship of different types of strain can be brought about through the work of deformation or the strain energy [21]. This determines the stress-strain relation to within an arbitrary hydrostatic pressure $p$

$$\sigma_i = -p + \frac{1}{\lambda_j \lambda_k} \cdot \frac{\partial W}{\partial \lambda_i},$$

(1.1)

where $\sigma_i$ are principal stresses, $\lambda_i$ are principal extension ratios (subscripts $j$ and $k$ indicate that these are different from $i$ and each other), and $W$ is the strain energy, that is evidently a function of principal stretches

$$W = W(\lambda_1, \lambda_2, \lambda_3).$$

(1.2)

This gives a very wide scope that the theory can cover, though we need it be sufficiently specific to be of real value. Rivlin [16] pointed out that the strain-energy function cannot be chosen completely arbitrary and considered certain requirements of logical consistency which determine at least some of its properties.

Firstly, the strain energy is unaltered by the rotation of deformed body, for instance, through $180^\circ$, which corresponds to a change of sign of two of the $\lambda$. This
implies that the strain energy must depend on only even powers of the \( \lambda \), then (1.2) is rewritten as

\[
W = W(\lambda_1^2, \lambda_2^2, \lambda_3^2).
\] (1.3)

Secondly, for isotropic materials in an unstrained state the strain energy is a symmetrical function in \( \lambda_1, \lambda_2, \lambda_3 \), having a form from which all directional distinction is absent, and thus it follows that the strain energy (1.3) can be expressed as

\[
W = W(I_1, I_2, I_3)
\] (1.4)

in terms of the following three invariants of the stretch tensor:

\[
I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2,
I_2 = \lambda_1^2\lambda_2^2 + \lambda_2^2\lambda_3^2 + \lambda_3^2\lambda_1^2,
I_3 = \lambda_1^2\lambda_2^2\lambda_3^2.
\] (1.5)

Assuming the incompressibility condition of rubberlike materials considered we have, further,

\[
\lambda_1\lambda_2\lambda_3 = 1,
\] (1.6)

we have, further,

\[
I_3 = 1, \text{ and } I_2 = 1/\lambda_1^2 + 1/\lambda_2^2 + 1/\lambda_3^2;
\] (1.7)

\[
W = W(I_1, I_2).
\] (1.8)

In the next section we present the eight-chain model derived by Arruda and Boyce.

### 1.3 The Arruda and Boyce eight-chain model

In this section we present a three-dimensional constitutive model derived by Arruda and Boyce for the large stretch behaviour of rubber elastic materials with the underlying macromolecular network structure that exhibits the non-Gaussian behaviour of its individual chains.
The simplest function of the strain energy that represents the Gaussian behaviour of individual chains within the macromolecular network structure of an isotropic, elastic material has the form

\[ W = \frac{1}{2} G (\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) = \frac{1}{2} G (I_1 - 3), \]

where \( G \) is a physical constant of the material (an elastic modulus).

However, the model proposed exploits Langevin chain statistics that is based upon the consideration of eight orientations of chains in space which may be envisioned by the eight chain network system sketched in Figure 1.1 for undeformed, uniaxial extension and biaxial extension loaded configurations.

![Figure 1.1: Eight-chain rubber elasticity model for (a) undeformed, (b) uniaxial extension and (c) biaxial extension configurations. Reproduced from [1].](image)

The use of Langevin statistics properly accounts for the limiting chain extensibility. The work of deformation \( W \) can be written in terms of the chain length \( r_{\text{chain}} \) in the form

\[ W = nk_B T N \left( \frac{r_{\text{chain}}}{Nl} \beta + \ln \frac{\beta}{\sinh \beta} \right) - Tc', \quad (1.9) \]

where \( n \) is the chain density, \( k_B \) is Boltzmann's constant, \( T \) is the temperature, \( N \) is the number of statistical links of length \( l \), \( \beta \) is the inverse Langevin function

\[ \beta = \frac{1}{\beta} \left[ r_{\text{chain}} / Nl \right], \quad (1.10) \]
which is defined as
\[ \mathcal{L}(\beta) = \coth \beta - (1/\beta), \]  
(1.11)
and \( c' \) is a constant.

The length of the initial chain \( r_0 \) is taken from a random walk consideration of \( N \) steps of length \( l \), and can be expressed as
\[ r_0 = \sqrt{N} l. \]  
(1.12)

The unstretched network includes eight chains of initial length (1.12) inside a cube of dimension \( a_0 \). From this geometry
\[ a_0 = \frac{2}{\sqrt{3}} r_0. \]  
(1.13)

Each chain is represented by a chain vector from the centre of the cube to a corner as shown in Figure 1.2.

Figure 1.2: The unstretched network of the eight-chain model. Reproduced from [1].

After the deformation the cube is stretched along the axes (its sides), which coincide with principal directions of strain, as shown in Figure 1.3. Then the chain vector
for a particular chain shown in Figure 1.3 may be written in the form

$$\vec{c}_1 = \frac{a_0}{2} \lambda_1 \hat{i} + \frac{a_0}{2} \lambda_2 \hat{j} + \frac{a_0}{2} \lambda_3 \hat{k}. \tag{1.14}$$

The length of this chain vector is equal to

$$r_{\text{chain}} = \frac{a_0}{2} (\lambda_1^2 + \lambda_2^2 + \lambda_3^2)^{1/2}. \tag{1.15}$$

All remaining chain vectors in the given configuration have the same lengths, namely (1.15), regardless of deformation state. Each chain in the system undergoes a stretch, \( \lambda_{\text{chain}} = r_{\text{chain}}/r_0 \), equivalent to that in every other network chain, and therefore the model is likened to averaging the contributions of a single chain over the eight spatial orientations.

![Figure 1.3: The eight-chain network in stretched mode. Reproduced from [1].](image)

In this form the expression for the chain vector length (1.15) is suitable for substitution into (1.9) which with (1.1) yields the following stress-stretch relation for the eight-chain model

$$\sigma_1 - \sigma_3 = \lambda_1 \frac{\partial W}{\partial \lambda_1} - \lambda_3 \frac{\partial W}{\partial \lambda_3} = \frac{n k_B T}{3} \sqrt{N} \Sigma^{-1} \left[ \frac{\lambda_{\text{chain}}}{\sqrt{N}} \right] \frac{\lambda_1^2 - \lambda_3^2}{\lambda_{\text{chain}}}. \tag{1.16}$$
Note that this formula (1.16) is given in [1] with $N$ in front of inverse Langevin function instead of its square root, $\sqrt{N}$, which is probably just an erratum.

The chain extension in this network model is given by a function of the root-mean-square of the applied stretches

$$\lambda_{\text{chain}} = \frac{1}{\sqrt{3}} (\lambda_1^2 + \lambda_2^2 + \lambda_3^2)^{1/2} = \frac{1}{\sqrt{3}} I_1^{1/2},$$

(1.17)

so that the strain energy of the eight-chain model appeared as a function of the first stretch invariant $I_1$ only.

Finally, the strain-energy function of this model may be found [1] through integration of (1.16) using the series expansion form for the Langevin function given for example in [22]. Herein, we cite the first five terms of this series expansion for the strain-energy function (1.9) of eight-chain model given at Arruda and Boyce [1]

$$W = nk_b T \left[ \frac{1}{2} (I_1 - 3) + \frac{1}{20N} (I_1^2 - 9) + \frac{11}{1050N^2} (I_1^3 - 27) \right] + nk_b T \left[ \frac{19}{7000N^3} (I_1^4 - 81) + \frac{519}{673750N^4} (I_1^5 - 243) + \ldots \right],$$

(1.18)

and it clearly exhibits the nonlinear dependence of the strain energy on first invariant of the stretch tensor, $I_1$.

In the next section we deal with the experimental data due to Treloar [20] and consider the standard deviations in its prediction by the eight-chain model.

1.4 The experimental data due to Treloar

At this stage we test the capability of the models in question to predict the stress-strain relations using the experimental data due to Treloar [20]. Therefore, in this section we present this data and explain the observed similarities between shear and uniaxial tensile behaviour and the differences in behaviour between equibiaxial and uniaxial tests.
Table 1.1: Values of engineering stresses $t$ correspondent to stretches $\lambda$ from Treloar's data on uniaxial extension, biaxial extension and pure shear.

<table>
<thead>
<tr>
<th>$\lambda$</th>
<th>$t$ (MPa)</th>
<th>$\lambda$</th>
<th>$t$ (MPa)</th>
<th>$\lambda$</th>
<th>$t$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.293</td>
<td>0.198</td>
<td>1.284</td>
<td>0.396</td>
<td>1.479</td>
<td>0.415</td>
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<td>1.414</td>
<td>0.283</td>
<td>1.690</td>
<td>0.632</td>
<td>1.861</td>
<td>0.599</td>
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<tr>
<td>1.601</td>
<td>0.382</td>
<td>1.959</td>
<td>0.750</td>
<td>2.341</td>
<td>0.779</td>
</tr>
<tr>
<td>1.886</td>
<td>0.482</td>
<td>2.463</td>
<td>0.972</td>
<td>2.968</td>
<td>0.935</td>
</tr>
<tr>
<td>2.155</td>
<td>0.600</td>
<td>3.089</td>
<td>1.237</td>
<td>3.505</td>
<td>1.105</td>
</tr>
<tr>
<td>2.440</td>
<td>0.661</td>
<td>3.480</td>
<td>1.463</td>
<td>3.986</td>
<td>1.276</td>
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<td>3.837</td>
<td>1.718</td>
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<td>3.628</td>
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<td>1.963</td>
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<td>5.433</td>
<td>1.951</td>
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<td>3.771</td>
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<td>7.328</td>
<td>4.883</td>
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<td>7.594</td>
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As shown in Figure 1.4, Treloar's data on the vulcanised 8% Sulphur rubber includes tests in uniaxial extension, biaxial extension and pure shear to very large stretches and are plotted as engineering stress versus extension ratio. The numerical values of engineering stress-strain points are presented in the Table 1.1.

Figure 1.4: Data from Treloar [20], plotted as engineering stress versus extension ratio in uniaxial extension, equibiaxial extension and pure shear.

Note should be made herein about the difference between engineering stress and true stress. The latter is the force on the test piece divided by the current cross-sectional area, whilst the former is the ratio of this force to the original cross-sectional area. Considering incompressible materials, the true stress can be easily obtained multiplying the engineering stress by the extension ratio. The rubber industry and
experimentalists (for instance, Kawabata's data [14]) traditionally measure engineering stresses, and the Treloar data presents the values of engineering stresses as well.

The data on biaxial extension in Figure 1.4 varies significantly from either uniaxial extension or pure shear data. This difference is due to the nature of the molecular chain stretching in equibiaxial extension versus uniaxial extension.

A biaxial extension

\[ \lambda_1 = \lambda, \quad \lambda_2 = \mu, \quad \lambda_3 = 1/\lambda \mu. \]  \hspace{1cm} (1.19)

offers two directions of principal tensile stretch. An initially isotropic network of chains will reach limiting chain extension due to stretching in both directions providing a planar state of orientation.

In uniaxial tensile deformation

\[ \lambda_1 = \lambda, \quad \lambda_2 = 1/\sqrt{\lambda}, \quad \lambda_3 = 1/\sqrt{\lambda} \]  \hspace{1cm} (1.20)

the chains extend along one direction only. Additional stretch is thus allotted through the drawing of material from the transverse direction, and the onset of limiting chain extension is delayed in juxtaposition with one in biaxial deformation.

The pure shear data is plotted (Figure 1.4) in terms of the maximum principal stretch, \( \lambda_1 \), versus the corresponding normal (not shear) engineering stress which acts in the direction of \( \lambda_1 \). Pure shear deformation

\[ \lambda_1 = \lambda, \quad \lambda_2 = 1, \quad \lambda_3 = 1/\lambda \]  \hspace{1cm} (1.21)

is more closely related to uniaxial extension than to equibiaxial one. The chain stretch occurs due to stretching along one principal direction with chains being drawn from one direction transverse to the extension direction in pure shear. Thus a pure shear experiment yields a limiting stretch value which is similar to that obtained in uniaxial extension.
The model that captures the observed similarities between shear and uniaxial tensile behaviour and the differences in behaviour between equibiaxial and uniaxial tests will satisfy our search.

Figure 1.5: Results of the eight-chain model by Arruda and Boyce [1] versus experimental data from Treloar [20] on uniaxial, biaxial extensions and pure shear.

On the basis of Treloar's experimental data [20] Arruda and Boyce compared [1] the predictive capability of their eight-chain model (1.16) with those of several prominent models: the three chain non-Gaussian model of Wang and Guth, the non-Gaussian tetrahedron model of Treloar, the well-known Mooney–Rivlin phenomenological model, the essentially empirical model of Ogden, and the Flory–Erman model of statistical mechanics which accounts for chain interactions.
The best fit with Treloar's data on uniaxial extension (standard deviation=4.452%) was obtained with parameters chosen as

\[ N = 26.5, \]

\[ \frac{nk_BT}{3} = 0.09245 \text{ J.} \]

Arruda and Boyce [1] illustrated the simplicity and effectiveness of their model over the earlier models. Only the Ogden model has been proved capable to better predict the mechanical response of rubber materials. However, in order to capture this nonlinear behaviour, it required six parameters in juxtaposition of only two of the eight-chain model.

The eight-chain model (1.16) predicts quite accurately (Figure 1.5) the response of rubberlike materials in uniaxial extension and pure shear and better than others in equibiaxial extension. However, there is still a considerable discrepancy between the prediction and experiment in equibiaxial deformation. The standard deviation between the Treloar experimental data and the simulation by eight-chain model in equibiaxial extension amounts to 20.1%, which is still excessive.

In the next section we assess the possibility to improve the results of the Arruda and Boyce eight-chain model. For this purpose we still regard the strain energy as a function dependent on the first invariant of the stretch tensor only, and thus evaluate the possibility to derive the strain-energy function which would give a better agreement with the Treloar experimental data in equibiaxial extension.

1.5 Comparison with the first stretch invariant model

The general form of a strain-energy function is represented by (1.8). The strain energy derived by Arruda and Boyce represents the behaviour of an isotropic, incompressible, rubber elastic material with the macromolecular network structure, that exhibits non-Gaussian behaviour of its individual chains, and has the form of (1.9). It is dependent
on only the first invariant of the stretch tensor \( I_1 \) and is clearly nonlinear (1.18) in it.

In this section we assess the predictive ability of the Arruda and Boyce model juxtaposing it with a model, whose strain energy is also a function of the first invariant of the stretch tensor only

\[ W = W(I_1), \quad (1.23) \]

and thus we shall regard the latter as the first stretch invariant model. In general, we evaluate the possibility to deduce the form of a strain-energy function (1.23) which would lead to a better agreement with the Treloar experimental data in equibiaxial extension.

As shown in the previous section (Figure 1.5) the simulation by the eight-chain model in uniaxial extension gives quite accurate agreement with the Treloar experimental data. Hence, it is reasonable to expect that the first stretch invariant model will do also well predicting engineering stresses in uniaxial deformation. Then the engineering stress (tensile force) in biaxial extension can be predicted theoretically on the basis of (1.1), (1.23), and available experimental data in uniaxial test.

Since the invariants of the stretch tensor are independent of the choice of coordinate system, it will be convenient for many purposes to proceed in terms of them. Hence the stress-strain relation (1.1), following the substitution of the strain-energy function (1.23), yields the expression

\[ \frac{dW}{dI_1}, \quad \frac{\partial I_1}{\partial \lambda_i} = -p + 2\lambda_1^2 \frac{dW}{dI_1} \quad (1.24) \]

in terms of the derivative of the strain energy with respect to the first stretch invariant.

In uniaxial extension

\[ \lambda_1 = \lambda_u > 1, \quad \lambda_2 = \lambda_3 = 1/\sqrt{\lambda_u} \quad (1.25) \]

(the subscript indicates the type of tension: \( u \) for uniaxial, \( b \) for biaxial) the principal stresses are given by

\[ \sigma_1 = 2(\lambda_u^2 - 1/\lambda_u)W'(I_u^1), \quad \sigma_2 = \sigma_3 = 0, \quad (1.26) \]
and the first stretch invariant has the form

$$I_1^u = \lambda_u^2 + 2/\lambda_u.$$  \hspace{1cm} (1.27)

The engineering stress $t(\lambda_u) = t_u$ corresponds to $\sigma_1/\lambda_u$, and the equation (1.26) gives

$$W'(I_1^u) = \frac{t_u}{2(\lambda_u - 1/\lambda_u^2)}. \hspace{1cm} (1.28)$$

We can find a principal extension ratio in equibiaxial extension

$$\lambda_1 = \lambda_2 = \lambda_u > 1, \ \lambda_3 = 1/\lambda_u^2$$ \hspace{1cm} (1.29)

such that it would give the first invariant of the stretch tensor

$$I_1^p = 2\lambda_u^2 + 1/\lambda_u^4$$ \hspace{1cm} (1.30)

with the same value as one in uniaxial extension (1.27). This will allow to calculate the principal stresses in this equibiaxial deformation through the formulae

$$\sigma_1 = \sigma_2 = 2(\lambda_u^2 - 1/\lambda_u^4)W'(I_1^u), \ \sigma_3 = 0,$$ \hspace{1cm} (1.31)

using the value for the derivative of the strain-energy function (1.28) found for uniaxial extension. The correspondent tensile force $t(\lambda_u) = t_u$ thus can be expressed as

$$t_u = \sigma_1/\lambda_u = 2(\lambda_u^2 - 1/\lambda_u^4)W'(I_1^u).$$ \hspace{1cm} (1.32)

To determine the value of an extension ratio in equibiaxial deformation with the first stretch invariant in uniaxial one we equate (1.27) with (1.30):

$$2\lambda_u^2 + 1/\lambda_u^4 = I_1^p = I_1^u = \lambda_u^2 + 2/\lambda_u.$$ \hspace{1cm} (1.33)

One of the roots of (1.33) corresponds to a biaxial compression

$$\lambda_u = \frac{1}{\sqrt[1]{\lambda_u}} < 1,$$ \hspace{1cm} (1.34)
Table 1.2: Engineering stresses $t_B$ (1.32) versus stretch $\lambda_B$ (1.35) in equibiaxial extension, determined using Treloar's experimental data $\lambda_u$, $t_u$ on uniaxial deformation.
being of no interest to us as the data does not refer to compression; another root, that we have actually looked for, corresponds to the equibiaxial extension

\[ \lambda_{B} = \frac{\lambda_{U}}{2} \left( 1 + \left( 1 + \frac{8}{\lambda_{U}^3} \right)^{1/2} \right)^{1/2} > 1, \quad (1.35) \]

while others are negative or complex, and are irrelevant in our consideration.

![Figure 1.6: Comparison of the results of the Arruda and Boyce (AB) eight-chain model (1.9) and of the first stretch invariant model (1.23) in predicting engineering stresses in equibiaxial test.](image)

Table (1.2) represents the experimental data in uniaxial extension \( \lambda_{U} \), \( t_{u} \) taken from Treloar [20], the values of the first stretch invariant \( I_{1}^{v} \) (1.27), and the derivative of the strain-energy function \( W'(I_{1}^{v}) \) (1.28), and corresponding to them the extension
ratio \( \lambda_b \) given by (1.35), and the value of the engineering stress \( t_b \) (1.32) in equibiaxial extension.

The two Figures 1.6 and 1.7 represent Treloar's points in biaxial experiment, the engineering stress in biaxial extension (Table 1.2) which is determined upon the assumption (1.23) and on the basis of Treloar's experimental data in uniaxial test (Table 1.1), and the corresponding points calculated by Arruda and Boyce from their eight-chain model for engineering force-extension relation in biaxial strain.

Figure 1.7: Comparison of the results of the Arruda and Boyce (AB) eight-chain model (1.9) and of the first stretch invariant model (1.23) in predicting engineering stresses in equibiaxial experiment against data of Treloar [20].

Apparently Arruda and Boyce did their utmost constructing a constitutive model on the basis of the strain energy (1.9), whose form is basically limited by (1.23). The
standard deviation between the results of their model and the prediction by the first stretch invariant model is only 6.8%. This indicates only a possibility of a slight improvement on the Arruda and Boyce results. The standard deviation between the Treloar experimental data and the prediction of the first stretch invariant model for equibiaxial extension will be still high (somewhat (%) from within the interval [18.9, 24.2]).

It follows from Figure 1.7 and the last argument that there was not much improvement using the strain energy of the form (1.23) compared with that derived by Arruda and Boyce (1.9).

The comparison of the eight-chain model [1] in question and the first stretch invariant model revealed that Arruda and Boyce had indeed achieved quite a remarkable approximation to the latter model. In order to capture more accurately the mechanical behaviour of rubberlike materials it is needed to consider a more general type of the strain-energy function (1.8) than limited by (1.23). In the next section we attempt to modify the Arruda and Boyce model by reducing the strain energy to the simple additive form of functions dependent on either first or second stretch invariant.

1.6 Modification of the strain energy into the additive form

In this section we assess the possibility to integrate the strain energy (1.9) derived for the eight-chain model within a general form of the strain-energy function (1.8). For this purpose we consider one of the simplest forms of the strain energy: the additive form of two functions, \( W_1 \) and \( W_2 \), that are dependent on either first or second invariant of the stretch tensor, \( I_1 \) or \( I_2 \),

\[
W(I_1, I_2) = W_1(I_1) + W_2(I_2). 
\]
In order to exploit the strain energy (1.9) derived by Arruda and Boyce, we adopt herein a quite simple and plausible assumption of a linear relation

\[ W_1(I_1) = \alpha W_{AB}(I_1) \]  

(1.37)

between the strain-energy function \( W_{AB}(I_1) \) derived by Arruda and Boyce (subscript \( AB \) relates to them and 1.9) and the first stretch invariant function \( W_1(I_1) \) of the amended model (1.36). Then to determine the parameter \( \alpha \) we need to use the experimental data on both uniaxial and equibiaxial extensions.

Recalling the stress-strain relation (1.1) and substituting there the additive form of the strain energy (1.36), the former transforms into the expression

\[ \sigma_i = -p + \lambda_i \frac{dW_1}{dI_1} \frac{\partial I_1}{\partial \lambda_i} + \lambda_i \frac{dW_2}{dI_2} \frac{\partial I_2}{\partial \lambda_i} \]  

(1.38)

in terms of the derivatives of the strain-energy functions by the first and second invariants of the stretch tensor, \( I_1 \) and \( I_2 \), correspondingly and then it reduces to

\[ \sigma_i = -p + 2\lambda_i^2 \frac{dW_1}{dI_1} - \frac{2}{\lambda_i^2} \frac{dW_2}{dI_2}. \]  

(1.39)

In uniaxial extension

\[ \lambda_1 = \lambda_u > 1, \quad \lambda_2 = \lambda_3 = 1/\sqrt{\lambda_u} \]  

(1.40)

the principal stresses are given by

\[ \sigma_1 = 2(\lambda_u^2 - 1/\lambda_u)[W_1'(I_1^u) + (1/\lambda_u)W_2'(I_2^u)], \quad \sigma_2 = \sigma_3 = 0, \]  

(1.41)

and the first and second stretch invariants have the form

\[ I_1^u = \lambda_u^2 + 2/\lambda_u, \quad I_2^u = 2\lambda_u + 1/\lambda_u^2. \]  

(1.42)

Since the eight-chain model gives quite accurate agreement with the Treloar experimental data in uniaxial extension, the value of the principal stress \( \sigma_1 \) given by (1.41)
should correspond to (1.26). This will allow to find the derivative of the unknown function \( W_2(I_2) \) at a particular \( I_2 = I_2' \) in terms of known \( W_{AB}(I_1) \) as

\[
W'_2(I_2') = (1 - \alpha)\lambda_W W'_{AB}(I_1').
\] (1.43)

Here the derivative of the strain-energy function \( W_{AB}(I_1) \) can be calculated at \( I_1 = I_1' \) either on the basis of the Treloar experimental data in uniaxial extension and (1.28). Alternatively it can be computed either through the derivative of the truncated series expansion (1.18), that approximates the exact expression (1.9) for the strain energy, or directly through the derivative of the latter given by

\[
W'_{AB}(I_1) = \frac{n k_b T}{3} \sqrt{N} \Lambda^{-1} \left[ \frac{\lambda_{\text{chain}}}{\sqrt{N}} \right] \frac{1}{2 \lambda_{\text{chain}}}. \] (1.44)

In equibiaxial extension

\[
\lambda_1 = \lambda_2 = \lambda_a > 1, \quad \lambda_3 = 1/\lambda_b^2
\] (1.45)

the first and second stretch invariants are

\[
I_1^a = 2\lambda_a^2 + 1/\lambda_a^4, \quad I_2^a = \lambda_a^4 + 2/\lambda_a^2,
\] (1.46)

and the principal stresses read

\[
\sigma_1 = \sigma_2 = 2(\lambda_a^2 - 1/\lambda_a^4)[W_1'(I_1^a) + \lambda_b^2 W_2'(I_2^a)], \quad \sigma_3 = 0.
\] (1.47)

Exploiting similar ideas to those from the previous section, we can find an extension ratio in uniaxial extension such that it would lead to the second stretch invariant given by (1.42) with the same value as one given by (1.46) in equibiaxial deformation. This will allow to calculate the principal stresses (1.47) for experimental points on equibiaxial strain, using the value for the derivative of the unknown function \( W_2(I_2) \) found in uniaxial extension (1.43).
To determine the value of an extension ratio in uniaxial deformation linked to one for equibiaxial strain in the manner prescribed above we equate the second stretch invariants in (1.42) and (1.46):

$$\lambda_2^n + 2/\lambda_2^2 = I_2^b = I_2^v = 2\lambda_v + 1/\lambda_v^2.$$  

(1.48)

One of the roots of (1.48) corresponds to a uniaxial compression

$$\lambda_u = \frac{1}{\lambda_b^2} < 1,$$  

(1.49)

another root, that we have actually looked for, corresponds to uniaxial extension

$$\lambda_u^* = \frac{\lambda_b^8}{4} \left(1 + \left(1 + \frac{8}{\lambda_b^8}\right)^{1/2}\right) > 1,$$  

(1.50)

while others are negative or complex, and are irrelevant in our consideration.

Consequently we write the engineering stress in equibiaxial extension as

$$t(\lambda_b) = \sigma_1/\lambda_b = 2(\lambda_b - 1/\lambda_b^5)[W'_1(I_1^b) + \lambda_b^2 W'_2(I_2^b)],$$  

(1.51)

where $W'_2(I_2^b)$ can be found through (1.43) and (1.50). Or putting

$$I_1^* = \lambda_u^* + 2/\lambda_u^*,$$

we can rewrite (1.51) on the basis of (1.37) and (1.43) in terms of $W'_{AB}(I_1)$ only

$$t(\lambda_b, \alpha) = 2(\lambda_b - 1/\lambda_b^5) \left[\alpha W'_{AB}(I_1^b) + (1 - \alpha)\lambda_b^2 \lambda_u^* W'_{AB}(I_1^b)\right].$$  

(1.52)

To find the parameter $\alpha$ we form the deviation function

$$D_{\text{abs}}(\alpha) = \frac{1}{N_\lambda} \sum_{\lambda_b} |t_{\exp}(\lambda_b) - t(\lambda_b, \alpha)|^2$$  

(1.53)

to employ the least squares best fit

$$\frac{d}{d\alpha} D_{\text{abs}}(\alpha) = 0,$$  

(1.54)
Table 1.3: Approximation of the parameter $\alpha$ by the number $N_\lambda$ of experimental points in equibiaxial extension taken into account in (1.55).

<table>
<thead>
<tr>
<th>Stretch</th>
<th>Function $W'_1(I_1^\mu)$</th>
<th>$I_2(\lambda_\mu) = I_2(\lambda_0^\mu)$</th>
<th>Function $W'_2(I_2^\mu)$</th>
<th>Param. $\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_\lambda$:</td>
<td>$\lambda_\mu$</td>
<td>$I_1^\mu \sim W'(I_1^\mu)$</td>
<td>$I_2^\mu$</td>
<td>$\lambda_0^\mu$</td>
</tr>
<tr>
<td>1: 1.284</td>
<td>3.665</td>
<td>0.157</td>
<td>3.931</td>
<td>1.814</td>
</tr>
<tr>
<td>2: 1.690</td>
<td>5.835</td>
<td>0.153</td>
<td>8.858</td>
<td>4.403</td>
</tr>
<tr>
<td>3: 1.959</td>
<td>7.743</td>
<td>0.146</td>
<td>15.249</td>
<td>7.616</td>
</tr>
<tr>
<td>4: 2.463</td>
<td>12.160</td>
<td>0.146</td>
<td>37.131</td>
<td>18.564</td>
</tr>
<tr>
<td>5: 3.089</td>
<td>19.095</td>
<td>0.155</td>
<td>91.258</td>
<td>45.629</td>
</tr>
<tr>
<td>6: 3.480</td>
<td>24.228</td>
<td>0.166</td>
<td>146.827</td>
<td>73.413</td>
</tr>
<tr>
<td>7: 3.837</td>
<td>29.450</td>
<td>0.180</td>
<td>216.890</td>
<td>108.445</td>
</tr>
<tr>
<td>8: 4.154</td>
<td>34.515</td>
<td>0.202</td>
<td>297.880</td>
<td>148.938</td>
</tr>
<tr>
<td>9: 4.365</td>
<td>38.109</td>
<td>0.213</td>
<td>363.130</td>
<td>181.565</td>
</tr>
<tr>
<td>10: 4.559</td>
<td>41.571</td>
<td>0.230</td>
<td>432.091</td>
<td>216.045</td>
</tr>
</tbody>
</table>

where $t_{\text{exp}}(\lambda_\mu)$ is the Treloar experimental point for the engineering stress in equibiaxial extension, $t(\lambda_\mu)$ is given by (1.52).

This gives the expression defining the parameter $\alpha$

$$\alpha = \sum_{\lambda_\mu} \frac{(\lambda_\mu - 1/\lambda_\mu^5) [W'_{\lambda\mu}(I_1^\mu) - \lambda_\mu^2 \lambda_0^\mu W'_{\lambda\mu}(I_1^\mu)] \{t_{\text{exp}}(\lambda_\mu) - 2(\lambda_\mu - 1/\lambda_\mu^5) \lambda_\mu^2 \lambda_0^\mu W'_{\lambda\mu}(I_1^\mu)\}}{\sum_{\lambda_\mu} 2(\lambda_\mu - 1/\lambda_\mu^5)^2 [W'_{\lambda\mu}(I_1^\mu) - \lambda_\mu^2 \lambda_0^\mu W'_{\lambda\mu}(I_1^\mu)]^2}.$$  

(1.55)

Table 1.3 clearly suggests that the assumption (1.36) together with (1.37) can work only up to $\lambda_\mu = 1.959$. If we take the deformation further then we will exceed the limiting material extensibility ($\lambda_0^\mu > 7.616$), and the parameter will tend to

$$\alpha = 1.000.$$  

(1.56)

This becomes more evident if we write down the approximate expression of the term
in square brackets in (1.52) on the basis of (1.50) as

\[ W'_1(I_1) + \lambda_b^2 W'_2(I_2) \approx \alpha W'_A(\lambda_b^A) + (1 - \alpha) \lambda_b^B W'_A(\lambda_b^B). \]  

(1.57)

The assumption (1.37) together with (1.43) and (1.56) gives

\[ W_1(I_1) = W_{AB}(I_1), \quad W_2(I_2) = 0, \]  

(1.58)

and this reduces the strain energy (1.36) of the amended model to that derived by Arruda and Boyce for the eight-chain model. This implies that we cannot improve the predictive capability of their model within these limitations (1.36), (1.37). The search continues.
Chapter 2

The Turner and Brennan composite model and its evaluation

In this chapter we turn our attention to the Turner and Brennan composite model, which combines the stresses due to the Poisson ratio approach and due to the filament theory. We have extended the prediction of stresses from the area of low strain, considered by Turner and Brennan, into the area of large stretches for the Kawabata experimental data [14] in uniaxial and equibiaxial extensions. Consequently the stresses in non-equibiaxial deformations have been predicted quite accurately. The agreement with the extensive experimental data due to Kawabata is very remarkable. And that alone gives strong support the model. To compare the predictive capability of the Arruda and Boyce eight-chain model and the composite model we have assessed the standard deviations of the latter in the simulation of the Treloar experimental data. The results obtained in this chapter suggests that it is advisable from the practical standpoint to exploit the composite model for the prediction of the mechanical behaviour of PVC materials. In the support of this recommendation the third chapter explores the prediction of the yield stress for oriented PVC.
2.1 Introduction

In the first chapter we studied the eight-chain model due to Arruda and Boyce. They derived a strain-energy function of outstanding quality for the rubber elastic materials with the underlying macromolecular network structure that exhibits non-Gaussian behaviour of its individual chains. This model exceeds the earlier models in the predictive capacity, though leaving the discrepancy in terms of the standard deviation of 20.1% between the prediction and equibiaxial experiments reported by Treloar. The attempts to improve their model did not have much success.

The other modelling in focus is the Turner and Brennan composite theory. In this chapter we evaluate its potential not only to improve the agreement with the equibiaxial experimental data due to Treloar but also to predict the extensive multiaxial experimental data due to Kawabata.

In contrast to the Arruda and Boyce model with its sophisticated chain statistics, the composite model is purely empirical. This, however, can turn out to be the advantage for we can modify it more easily than the eight-chain model and to whatever extent we may want.

The composite model is the combination of Poisson’s ratio approach, discussed in some detail in the next section, and filament theory. Turner and Brennan based their model on a single filament only as against the eight-chain configuration in the Arruda and Boyce model. Their argument is that each filament of the microstructure undergoes the same spatial deformation, so that it is quite appropriate to base the model on only a single filament.

The Poisson ratio approach copes easily within the area of low stretches. Turner and Brennan reproduced the Kawabata experimental data in uniaxial and equibiaxial extensions for that region of deformations.

In this chapter we extend their predictions to the range of large elastic strains.
Consequently we predict stresses in non-equibiaxial deformation and compare the results with the extensive Kawabata data on it. Also we produce some arguments about the limitations on the composite model parameters.

We start by briefly reviewing the behaviour of a filament extension and tension in it, pointing out the areas of dominance by the stresses due to the Poisson's ratio approach and by those that arise from the filament theory. Hence Young's modulus can be chosen by fitting the curve in the area of low strain, which reduces to a simple and tangible procedure. Then we propose a method to determine the parameter that describes the limit to extensibility. It is based on the numerical minimisation of the standard deviation of the prediction from the Kawabata experimental data in uniaxial and equibiaxial deformations collectively. The third parameter of the composite model, the filament modulus, is determined as a by-product of least squares best fit for the standard deviation minimised to find maximum extensibility.

Also we identified those values of parameters that allow us to keep the fairly reasonable agreement between the predictions of the composite model in both uniaxial and equibiaxial extensions and Treloar's experimental data. Thus our evaluation, based on the standard deviations in uniaxial and equibiaxial extensions from the Treloar data, advises us to exploit the composite model in the study and characterisation of the mechanical behaviour of oriented PVC material.

2.2 The Poisson ratio approach

In this section we present a Poisson's ratio approach, which is due to Turner and Brennan [24]. We start with some well-known low strain equations for the stress in isotropic, incompressible, elastic materials, and then transform them utilising a variable Poisson's ratio.

The stress-strain relations [24] normally used in the region of low strain for
isotropic, elastic materials are well-known and read

\[
\begin{align*}
\lambda_1 - 1 &= \frac{\sigma_1 - \nu(\sigma_2 + \sigma_3)}{E}, \\
\lambda_2 - 1 &= \frac{\sigma_2 - \nu(\sigma_3 + \sigma_1)}{E}, \\
\lambda_3 - 1 &= \frac{\sigma_3 - \nu(\sigma_1 + \sigma_2)}{E},
\end{align*}
\]

(2.1)

where \(E\) is Young's modulus, and \(\nu\) is Poisson's ratio.

The application of hydrostatic pressure does not affect the elongations in the equations (2.1) when the Poisson ratio \(\nu\) has the value of 0.5, i.e. at infinitesimal strains. True stresses are expressed through hydrostatic pressure, \(p\), as

\[
\sigma_i = -p + \sigma'_i,
\]

where \(\sigma'_i\) are deviatoric stresses. Then, assuming that \(\sigma_3 = -p + \sigma'_3 = 0\) as it usually is and taking into account that \(\sigma'_1 - \sigma'_3 = \sigma_1 - \sigma_3\) and \(\sigma'_2 - \sigma'_3 = \sigma_2 - \sigma_3\), the equations (2.1) can be restated in the form

\[
\begin{align*}
\lambda_1 - 1 &= \frac{\sigma_1 - \sigma_3 - \nu(\sigma_2 - \sigma_3)}{E}, \\
\lambda_2 - 1 &= \frac{\sigma_2 - \sigma_3 - \nu(\sigma_1 - \sigma_3)}{E}, \\
\lambda_3 - 1 &= -\nu((\sigma_1 - \sigma_3) + (\sigma_2 - \sigma_3))/E,
\end{align*}
\]

(2.2)

in which hydrostatic pressure has no effect on elongations whatever the value of the Poisson ratio. These equations (2.2) were first written in terms of deviatoric stresses.

Considering now the Poisson ratio to be variable, i.e. a function of \(\lambda_1\) and \(\lambda_2\), and utilising it in (2.2), we deduce the following relations

\[
\begin{align*}
\sigma_1 - \sigma_3 &= E \frac{\lambda_1 - 1 + \nu(\lambda_2 - 1)}{1 - \nu^2}, \\
\sigma_2 - \sigma_3 &= E \frac{\lambda_2 - 1 + \nu(\lambda_1 - 1)}{1 - \nu^2}, \\
\nu &= \frac{\lambda_1 \lambda_2 - 1}{\lambda_1 \lambda_2 (\lambda_1 + \lambda_2 - 1) - 1}.
\end{align*}
\]

(2.3)

These give a linear relation in uniaxial extension but a nonlinear one in biaxial strain, that is due to a variable Poisson's ratio.
Turner and Brennan [24] applied the Poisson ratio approach to predict the experimental data due to Kawabata for the area of low extension ratios. However, from their paper [24] itself it is not clear if they used the formulation (2.3) or its analogue for incremental stresses: “It can, however, be successful if it is used for a series of increments in extension, with each extension providing the basis for the next extension stage.” If the latter then the equations they used would be

\[ \Delta \sigma_1 = E \frac{\Delta \lambda_1 + \nu \Delta \lambda_2}{1 - \nu^2}, \]
\[ \Delta \sigma_2 = E \frac{\Delta \lambda_2 + \nu \Delta \lambda_1}{1 - \nu^2}, \]  
\[ \nu = \frac{\lambda_1 \lambda_2 - 1}{\lambda_1 \lambda_2 (\lambda_1 + \lambda_2 - 1) - 1}. \]  

(2.4)

where \( \Delta \) denotes the increment in the quantity and is to be added to the current value. Note that Poisson's ratio \( \nu \) is still given by the same formula and is expressed in terms of current values of the stretches.

To implement the incremental scheme (2.4) and to keep the results in consistency with \( \sigma_2 = \sigma_3 = 0 \) in uniaxial extension, we demand

\[ \Delta \sigma_2 = E \frac{\Delta \lambda_2 + \nu \Delta \lambda_1}{1 - \nu^2} = 0. \]

(2.5)

Then the increments are related by

\[ \Delta \lambda_2 = -\nu \Delta \lambda_1, \]

(2.6)

and this results in the formula for the stress as

\[ \Delta \sigma_1 = E \frac{\Delta \lambda_1 - \nu^2 \Delta \lambda_1}{1 - \nu^2} = E \Delta \lambda_1, \]

(2.7)

which yields exactly the same expression if derived directly from (2.3)

\[ \sigma_1 = E (\lambda_1 - 1). \]

(2.8)
Otherwise, if (2.6) does not hold, there is an inconsistency in a nonzero value of $\sigma_2$:

$$\sigma_2 - \sigma_3 \neq 0.$$  \hfill (2.9)

Although the consistency in equibiaxial extension ($\sigma_1 = \sigma_2$) preserves if

$$\Delta \lambda_1 = \Delta \lambda_2,$$  \hfill (2.10)

and then the incremental stresses are of the form

$$\Delta \sigma_1 = \Delta \sigma_2 = E \frac{\Delta \lambda_1 + \nu \Delta \lambda_1}{1 - \nu^2} = E \frac{\Delta \lambda_1}{1 - \nu},$$  \hfill (2.11)

this will change the nonlinear behaviour of the direct scheme (2.3) because Poisson's ratio varies at different steps now.

To find out which of these two formulations (2.3), (2.4) they used, we reproduce both of them and compare the results with the Kawabata experimental data. Our findings on this we report in the next section. Anticipating the results, we should point out that the formulation (2.3) of the Poisson's ratio approach should be used.

In the next section we present the extensive multiaxial data on isoprene rubber vulcanisate published by Kawabata [14].

### 2.3 The experimental data due to Kawabata

This section lists the experimental results published by Kawabata et al. [14], and regarded by us throughout this work simply as the experimental data due to Kawabata. They performed extensively not only uniaxial and equibiaxial tests but also non-equibiaxial ones. The section also contains some preliminary results on the prediction of the data obtained in these experiments, that reproduce the work of Turner and Brennan [24] at low strain area on the basis of the Poisson's ratio approach. The area of large stretches will be dealt in the later sections.
<table>
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Table 2.1: The Kawabata experimental data (MPa) for Isoprene Rubber Vulcanisate in biaxial strain at $T = 293$ K. (Continued on the next page.)
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Table 2.1: The Kawabata experimental data (MPa) for Isoprene Rubber Vulcanisate in biaxial strain at $T = 293$ K. (Continued on the next page.)
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Experimentalists (for instance, Treloar's data) traditionally measure engineering stresses (normal tensile force acting on the initial area), and the Kawabata data is not an exception: it lists the values of engineering stresses (Table 2.1) as well. Theoreticians, however, usually operate with true stresses since this way we separate material behaviour from geometrical effects. Therefore, the experimental points due to Kawabata have been recalculated into true stresses, which we present on the plots.

First, we repeat their results modelling the behaviour of the rubber material in uniaxial and equibiaxial extensions reported by Kawabata. In our calculations we use the value of Young's modulus

\[ E = 1.1354 \text{ MPa} \]


\[ \text{(2.12)} \]

Figure 2.1: True stresses predicted by the Poisson's ratio approach (2.3), which coincides in uniaxial extension with the incremental scheme (2.11), against the Kawabata experimental data (\(\bullet\)).

Figure 2.1 represents the results of direct formulation (2.3) in uniaxial extension versus the Kawabata data (the results of consistent incremental scheme (2.7) coincide with those of direct formulæ (2.8)).
The results of the direct formulation (2.3) give the following curve (Figure 2.2) against the Kawabata data in equibiaxial extension.

![Figure 2.2: True stresses predicted by the Poisson's ratio approach (2.3) in equibiaxial extension against the Kawabata experimental data (*)](image)

The results of the incremental scheme (2.11) are presented by a dashed line against the Kawabata data in equibiaxial extension in Figure 2.3.

![Figure 2.3: The results of incremental scheme (2.11) against the Kawabata experimental data (*) in equibiaxial extension.](image)

Figure 2.4 shows two latter plots together for the comparison. It appears that the direct formulae (2.3) of the Poisson's ratio approach give the more accurate agreement with the experimental data given by Kawabata than its incremental scheme (2.4).
Figure 2.4: The results of direct Poisson’s ratio simulation (solid) and incremental scheme (dashed) against the Kawabata experimental data (●) in equibiaxial extension.

Figures 2.1 and 2.2 imply that the prediction on the basis of the Poisson’s ratio approach (2.3) agrees quite reasonably with the Kawabata experimental data in uniaxial and equibiaxial extensions in the area of low stretches.

If we now extend the prediction into the area of larger stretches by the Poisson’s ratio approach, then the agreement with the Kawabata experimental data in uniaxial (Figure 2.5) and equibiaxial (Figure 2.6) deformations deteriorates. It is not surprising for the formulation of the Poisson’s ratio approach (2.3) utilises just a single material constant.

Figure 2.5: The results of direct Poisson’s ratio simulation (2.3) against the Kawabata experimental data (●) in the area of large uniaxial extension.
Turner has pointed out in his talk [23] at a workshop in Oxford that the results can be improved taking into account the residual stress, that arises through the tension in the microstructure of rubberlike materials. For that purpose he proposes to exploit the filament theory. The next section deals with its particulars.

2.4 The filament theory and the composite model

In this section we give the description of the filament theory, that has been proposed by Turner [23] to account for large strain deformations in rubberlike materials. This one together with the Poisson’s ratio approach forms the basis of the composite model.

Turner and Brennan [24] proposed to use the Poisson’s ratio approach to predict the low strain deformations in elastic materials requiring only a single material constant. It works well for the mentioned range of deformation, but starts to deviate significantly in the area of large strain. In his talk Turner [23] has invited us to extend the model into the area of large strains using the same concept that Arruda and Boyce used but observing the orientation of only one filament.

The angle (Figure 2.7) between the corner to corner line and the direction of the...
extension defined as
\[ \tan \alpha_1 = \sqrt{\frac{\lambda_3^2 + \lambda_2^2}{\lambda_1^2}} \]  
\[ (2.13) \]

serves as the parameter that describes the orientation achieved in drawing.

The tension in a filament \( t_f \) is given [23] by the expression
\[ t_f = E_f \frac{e}{1 - e/e_{\text{max}}}, \]
\[ (2.14) \]
in which \( E_f \) is the elasticity parameter of the filament, \( e_{\text{max}} \) is the limit of extensibility, which is quantified by the extension of a filament, \( e \), that reads
\[ e = \sqrt{\frac{\lambda_3^2 + \lambda_2^2 + \lambda_1^2}{3}} - 1. \]
\[ (2.15) \]

Note that the expression (2.14) does not have any statistical basis, it is purely empirical, and thus the whole theory is merely empirical. Although there is some advantage in this: you can amend the model in whatever way you may want to.
The filament extension (2.15) is a function of the first invariant of the stretch tensor only and can be expressed in terms of \( \lambda_{\text{chain}} \) given by (1.17) as \( e = \lambda_{\text{chain}} - 1 \). Turner [23] has approximated the behaviour of the inverse Langevin function present in (1.16) by a simple expression for the filament tension (2.14). Hence, filament theory has to some extent a similar concept as the eight-chain model [1].

Note that the axes of principal strain coincide with sides of parallelepiped (Figure 2.7). The principal stresses are given by the relations \( \sigma_{if} = \lambda_i t_{if} \), where \( t_{if} \) are engineering stresses. The latter can be found from the bulk resolution of tensile forces that in deformed configuration reads

\[
t_{1f} \vec{t} + t_{2f} \vec{j} + t_{3f} \vec{k} = t_f \vec{e},
\]

where the vector along the diagonal is equal to \( \vec{e} = \cos \alpha_1 \vec{t} + \cos \alpha_2 \vec{j} + \cos \alpha_3 \vec{k} \).

Then the true stresses for the filament model may be expressed in the form

\[
\sigma_{if} = \lambda_1 \cos \alpha_1 \ t_f,
\]

\[
\sigma_{2f} = \lambda_2 \cos \alpha_2 \ t_f,
\]

\[
\sigma_{3f} = \lambda_3 \cos \alpha_3 \ t_f,
\]

in which \( \cos \alpha_i \), being defined in the manner of (2.13), read

\[
\cos \alpha_i = \frac{\lambda_i}{\sqrt{\lambda_1^2 + \lambda_2^2 + \lambda_3^2}}. \tag{2.17}
\]

The principal stresses (2.16) for the filament model together with the principal stresses (2.3) defined through the Poisson's ratio approach constitute the composite model for rubberlike materials

\[
\begin{align*}
\sigma_1 - \sigma_3 &= E \left( \frac{\lambda_1 - 1 + \nu(\lambda_2 - 1)}{1 - \nu^2} \right) + \left( \lambda_1 \cos \alpha_1 - \lambda_3 \cos \alpha_3 \right) \frac{E_f e}{1 - e/e_{\text{max}}}, \\
\sigma_2 - \sigma_3 &= E \left( \frac{\lambda_2 - 1 + \nu(\lambda_1 - 1)}{1 - \nu^2} \right) + \left( \lambda_2 \cos \alpha_2 - \lambda_3 \cos \alpha_3 \right) \frac{E_f e}{1 - e/e_{\text{max}}}, \\
\nu &= \frac{\lambda_1 \lambda_2 - 1}{\lambda_1 \lambda_2 (\lambda_1 + \lambda_2 - 1) - 1}.
\end{align*} \tag{2.18}
\]
The composite model (2.18) possesses three material parameters: Young's modulus $E$, the filament modulus $E_f$, and the limit to extensibility $e_{\text{max}}$. It exhibits a nonlinear behaviour of engineering stresses in deformation, and Poisson's ratio is not a material constant by a variable.

In the next section we extend the prediction of the Kawabata experimental data in uniaxial and biaxial tests into the area of large strains.

### 2.5 Prediction of the stress in uniaxial and equibiaxial extensions

In this section we give the prediction to the Kawabata experimental results in uniaxial and biaxial tests extended into the area of large strains. For that purpose we also consider the methods used to choose the three parameters for the composite model: Young's modulus $E$, the filament modulus $E_f$, and the limit to extensibility $e_{\text{max}}$.

The Figure 2.8 represents the behaviour of a reduced filament tension, $t_f/E_f$, with $e_{\text{max}}$ taken from (2.25).

![Figure 2.8: The growth of a reduced filament tension in uniaxial (solid) and equibiaxial (dashed) deformations.](image)

The orientation of the filament makes the true stress initially proportional to the
square of the extension ratio. Then ultimately the stress rises steeply due to the term with $e_{\text{max}}$. Note that shapes of two curves in Figure 2.8 replicate those of correspondent curves in Figure 1.5. This resemblance arises from a close approximation of the inverse Langevin function by (2.14).

Figure 2.8 clearly suggests that in the area of low strain the stress due to the Poisson's ratio approach plays the dominant role, and then further the filament theory starts to affect the composite model significantly. Therefore, Young's modulus $E$ can be found on the basis of the experimental data in the area of low stretches, and thus we may stick to Young's modulus (2.12) determined by Turner and Brennan [24].

The method to identify the limit to extensibility, $e_{\text{max}}$, is not that straightforward. Figure 2.9 compares the growth of the filament extension (2.15) in uniaxial and equibiaxial strains.

Figure 2.9: The behaviour of a filament extension (2.15) in uniaxial (solid) and equibiaxial (dashed) deformations.

Testing the extensibility of a material up to its limit, the physical constant $e_{\text{max}}$ can be determined experimentally, and this would give truly a physical meaning to the material constant. That needs, of course, an additional experimental study.

Alternatively the value of the maximum extensibility can be chosen ad hoc for a particular set of experimental data (not a material). Theoretically, the parameter
could be determined through the least squares best fit applied to the standard deviation function of the filament modulus, $E_t$, and the limit to extensibility, $e_{\text{max}}$, in the manner similar to described below (2.20)–(2.24). However, the relations deduced are quite complicated and the solution to those is not obvious since the extensibility limit comes nonlinearly into the expression for the tensile force (2.14) and stands adjacent to another material parameter, the filament modulus.

Therefore, it is our understanding that first it is necessary to identify the limitations on the filament extension on the basis of the experimental data available. This leads to a restriction on the parameter as follows

$$\max_{\lambda} e < e_{\text{max}},$$

which prevents the infinite growth of the stress to happen before and when the largest stretch from the available experimental data occurs. Secondly, the filament modulus $E_t$ can be found minimising the deviation function (square of the S.D.)

$$D_{\text{rel}}(E_t) = \frac{1}{N_\lambda} \sum_{\lambda} \frac{[\sigma_{\text{exp}}(\lambda) - \sigma(\lambda, E_t)]^2}{\sigma_{\text{exp}}^2(\lambda)},$$

($N_\lambda$ is a number of points), for each value of $e_{\text{max}}$ varied within the interval

$$1.01 \cdot \max_{\lambda} e \leq e_{\text{max}} \leq 2.00 \cdot \max_{\lambda} e.$$

That way we can manage to numerically obtain the extremum points of the extensibility limit correspondent to the minimum value of the standard deviation within the above-mentioned segment, and this may be implemented in the appropriate environment like Mathematica 4.1 developed by Wolfram Research.

The expression (2.20) can be reduced to the form

$$D_{\text{rel}}(E_t) = \frac{1}{N_\lambda} \sum_{\lambda} \frac{[\sigma_t(\lambda) - A(\lambda, E_t)]^2}{\sigma_{\text{exp}}^2(\lambda)},$$

(2.21)
in which we put

\[
\sigma^r_0(\lambda) = \sigma_{\text{exp}}(\lambda) - [\sigma_{1p}(\lambda) - \sigma_{3p}(\lambda)],
\]

\[
\sigma_{1f}(\lambda, E_t) - \sigma_{3f}(\lambda, E_t) = A(\lambda) E_t,
\]

\[
A(\lambda) = \frac{(\lambda_1 \cos \alpha_1 - \lambda_3 \cos \alpha_3) e}{1 - e/e_{\text{max}}},
\]

where the subscript \(p\) relates to a stress defined by the Poisson's ratio approach (2.3). Subsequently from the least squares best fit

\[
\frac{d}{dE_t} D_{\text{rel}}(E_t) = 0
\]

the filament modulus \(E_t\) can be obtained as

\[
E_t = \frac{\sum_\lambda \sigma^r_0(\lambda) A(\lambda)/\sigma_{\text{exp}}^2(\lambda)}{\sum_\lambda A^2(\lambda)/\sigma_{\text{exp}}^2(\lambda)}.
\]

Minimisation of the deviation function (2.21) can be carried out on the basis of data either on one type of a (uniaxial or equibiaxial) test or on both collectively.

![Figure 2.10: The standard deviation between the prediction of the composite model (2.18) in uniaxial extension and Kawabata's experimental data.](image)

The standard deviation between the experimental data and the prediction in equibiaxial deformation calculated with parameters determined on the basis of uniaxial data alone (Figure 2.10) is higher than 7.140% for the whole range of \(e_{\text{max}}\).
Figure 2.11: The standard deviation between the prediction of the composite model (2.18) in equibiaxial extension (solid) and Kawabata's experimental data; and with the same parameters in uniaxial extension (dashed).

Interestingly, both solid curves (Figures 2.10 and 2.11) have the minima within the similar area of $e_{\text{max}}$, although standard deviations at a minimum are completely different and correspond to different filament moduli.

Figure 2.12: The standard deviation in the prediction by the composite model (2.18) of true stresses from the Kawabata experimental data in uniaxial and equibiaxial extensions collectively.

If we choose the value of $e_{\text{max}}$ giving the minimum of the standard deviation in uniaxial test (Figure 2.10) then the standard deviation in equibiaxial deformation would be high (S.D.=11.810%). And vice versa: if we choose the value of $e_{\text{max}}$ giving the minimum of the standard deviation in equibiaxial experiment (Figure 2.11) then
the standard deviation in uniaxial strain would also be relatively big (S.D.= 6.593%).

Therefore, we present the values of the limit to extensibility and filament modulus,

\[ e_{\text{max}} = 2.1967, \]

\[ E_f = 0.0831 \text{ MPa}, \]  

(2.25)

subsequently found on the basis of the least squares best fit (2.24), which gives the least standard deviation in uniaxial and equibiaxial tests collectively (Figure 2.12).

Figure 2.13: The prediction of the true stress by the composite model (2.25) in uniaxial extension versus the Kawabata experimental data (●). (S.D.= 3.806%).

Figure 2.14: The prediction of the true stress by the composite model (2.25) in equibiaxial extension versus the Kawabata experimental data (●). (S.D.= 5.944%).

This set of parameters (2.25) yields the standard deviations of 3.806% in uniaxial experiment (Figure 2.13) and of 5.944% in equibiaxial test (Figure 2.14).
Though the accuracy of the prediction on the Kawabata experimental data is already high, we can try and look for the improvement in equibiaxial strain. Since the composite model is purely empirical, we can modify it by adding a complementary term, which could correlate the error, in the expression for filament tension

\[ t_f = (E_0 + E_1 \epsilon) \frac{e}{1 - \epsilon/e_{\text{max}}} \]  

(2.26)

here \( E_0 \) and \( E_1 \) are new elasticity parameters entered instead of one \( E_t \) previously (2.14). The parameters of (2.26) can be determined with the value of \( E \) (2.12) by analogous procedure to one described above that led to a set (2.25). That will give

\[ e_{\text{max}} = 3.0637, \]
\[ E_0 = 0.0093 \text{ MPa}, \]
\[ E_1 = 0.0931 \text{ MPa}. \]  

(2.27)

This set of parameters for the amended model yields in the standard deviations of 3.820% in uniaxial experiment (Figure 2.15) and 5.411% in equibiaxial test (Figure 2.16). Though the standard deviation is improved in equibiaxial deformation, this has been achieved at the expense of the standard deviation in uniaxial test.

![Figure 2.15: The prediction of the amended composite model (2.26) in uniaxial extension versus the Kawabata experimental data.](image)

(S.D.=3.820%.)
Thus the composite model proposed by Turner [23] provides a reasonable and competitive agreement with the experimental data in uniaxial and equibiaxial tests.

If this section has mainly concentrated its attention on the procedure of choosing the set of material constants, the next one provides a real test for the composite model.

2.6 Model evaluation in non-equibiaxial extension

We are now ready to give the main result of this chapter, which is quite intriguing and promising.

Having determined the set of parameters (2.12), (2.25) that gives the best agreement with the Kawabata experimental data on uniaxial and equibiaxial extensions, we are now in the position to check the predictions of the composite model in non-equibiaxial strain. Fortunately, for this purpose plenty of data is available in Kawabata's paper (section 2.3).

Keeping the stretch in one direction, $\lambda_1$, constant we vary the stretch in the second direction, $\lambda_2$, between its values in uniaxial and equibiaxial deformations. Now we have to predict two principal stresses, $\sigma_1$ and $\sigma_2$. 

Figure 2.16: The prediction of the amended composite model (2.26) in equibiaxial extension versus the Kawabata experimental data (•). (S.D.=5.411%).

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Figure 2.16: The prediction of the amended composite model (2.26) in equibiaxial extension versus the Kawabata experimental data (•). (S.D.=5.411%).
The evaluation has been performed for $\lambda_1 \geq 1.3$ for we are most interested, of course, in the area of large strains.

![Graph](image1)

Figure 2.17: The prediction of the true stress by the composite model (2.18) in non-equibiaxial extension, $\sigma_1$, versus the Kawabata experimental data (●) at the constant stretch $\lambda_1 = 1.3$.

The standard deviation of the stress $\sigma_1$ predicted by the composite model in non-equibiaxial deformation at the constant stretch $\lambda_1 = 1.3$ constitutes $1.608\%$.

![Graph](image2)

Figure 2.18: The prediction of the true stress by the composite model (2.18) in non-equibiaxial extension, $\sigma_2$, versus the Kawabata experimental data (●) at the constant stretch $\lambda_1 = 1.3$.

The standard deviation of the stress $\sigma_2$ predicted by the composite model in non-equibiaxial deformation at the constant stretch $\lambda_1 = 1.3$ constitutes $1.743\%$. 
Figure 2.19: The prediction of the true stress by the composite model (2.18) in non-equibiaxial extension, $\sigma_1$, versus the Kawabata experimental data (●) at the constant stretch $\lambda_1 = 1.6$.

The standard deviation of the stress $\sigma_1$ predicted by the composite model in non-equibiaxial deformation at the constant stretch $\lambda_1 = 1.6$ constitutes 4.012%.

Figure 2.20: The prediction of the true stress by the composite model (2.18) in non-equibiaxial extension, $\sigma_2$, versus the Kawabata experimental data (●) at the constant stretch $\lambda_1 = 1.6$.

The standard deviation of the stress $\sigma_2$ predicted by the composite model in non-equibiaxial deformation at the constant stretch $\lambda_1 = 1.6$ constitutes 4.764%.
Figure 2.21: The prediction of the true stress by the composite model (2.18) in non-equibiaxial extension, $\sigma_1$, versus the Kawabata experimental data (•) at the constant stretch $\lambda_1 = 1.9$.

The standard deviation of the stress $\sigma_1$ predicted by the composite model in non-equibiaxial deformation at the constant stretch $\lambda_1 = 1.9$ constitutes 5.001%.

Figure 2.22: The prediction of the true stress by the composite model (2.18) in non-equibiaxial extension, $\sigma_2$, versus the Kawabata experimental data (•) at the constant stretch $\lambda_1 = 1.9$.

The standard deviation of the stress $\sigma_2$ predicted by the composite model in non-equibiaxial deformation at the constant stretch $\lambda_1 = 1.9$ constitutes 6.786%.
Figure 2.23: The prediction of the true stress by the composite model (2.18) in non-equibiaxial extension, $\sigma_1$, versus the Kawabata experimental data (●) at the constant stretch $\lambda_1 = 2.2$.

The standard deviation of the stress $\sigma_1$ predicted by the composite model in non-equibiaxial deformation at the constant stretch $\lambda_1 = 2.2$ constitutes 4.362%.

Figure 2.24: The prediction of the true stress by the composite model (2.18) in non-equibiaxial extension, $\sigma_2$, versus the Kawabata experimental data (●) at the constant stretch $\lambda_1 = 2.2$.

The standard deviation of the stress $\sigma_2$ predicted by the composite model in non-equibiaxial deformation at the constant stretch $\lambda_1 = 2.2$ constitutes 7.811%.
Figure 2.25: The prediction of the true stress by the composite model (2.18) in non-equibiaxial extension, $\sigma_1$, versus the Kawabata experimental data (●) at the constant stretch $\lambda_1 = 2.5$.

The standard deviation of the stress $\sigma_1$ predicted by the composite model in non-equibiaxial deformation at the constant stretch $\lambda_1 = 2.5$ constitutes 3.345%.

Figure 2.26: The prediction of the true stress by the composite model (2.18) in non-equibiaxial extension, $\sigma_2$, versus the Kawabata experimental data (●) at the constant stretch $\lambda_1 = 2.5$.

The standard deviation of the stress $\sigma_2$ predicted by the composite model in non-equibiaxial deformation at the constant stretch $\lambda_1 = 2.5$ constitutes 8.454%.
Figure 2.27: The prediction of the true stress by the composite model (2.18) in non-equibiaxial extension, $\sigma_1$, versus the Kawabata experimental data (●) at the constant stretch $\lambda_1 = 2.8$.

The standard deviation of the stress $\sigma_1$ predicted by the composite model in non-equibiaxial deformation at the constant stretch $\lambda_1 = 2.8$ constitutes 3.728%.

Figure 2.28: The prediction of the true stress by the composite model (2.18) in non-equibiaxial extension, $\sigma_2$, versus the Kawabata experimental data (●) at the constant stretch $\lambda_1 = 2.8$.

The standard deviation of the stress $\sigma_2$ predicted by the composite model in non-equibiaxial deformation at the constant stretch $\lambda_1 = 2.8$ constitutes 9.593%.
Figure 2.29: The prediction of the true stress by the composite model (2.18) in non-equibiaxial extension, $\sigma_1$, versus the Kawabata experimental data (•) at the constant stretch $\lambda_1 = 3.1$.

The standard deviation of the stress $\sigma_1$ predicted by the composite model in non-equibiaxial deformation at the constant stretch $\lambda_1 = 3.1$ constitutes 9.075%.

Figure 2.30: The prediction of the true stress by the composite model (2.18) in non-equibiaxial extension, $\sigma_2$, versus the Kawabata experimental data (•) at the constant stretch $\lambda_1 = 3.1$.

The standard deviation of the stress $\sigma_2$ predicted by the composite model in non-equibiaxial deformation at the constant stretch $\lambda_1 = 3.1$ constitutes 11.248%.
The collection of Figures 2.17–2.30 shows a very accurate agreement of the composite model and the Kawabata experimental data in non-equibiaxial deformation. Note that some of the figures have completely different scales and therefore attention needs to be paid to the numerical values of standard deviations mentioned there.

The agreement between the prediction of the composite model and the Kawabata experimental results in non-equibiaxial deformation has been examined on the basis of preliminarily chosen set of parameters (2.12), (2.25) obtained from data on uniaxial and equibiaxial extensions. This gives the confidence to exploit the composite model predicting the nonlinear elastic behaviour of rubberlike materials and to proceed to the modelling the yield stress of oriented PVC in the last chapter.

The last section of this chapter is devoted to a comparison of standard deviations in the prediction of the Treloar experimental data by the composite model and the eight-chain model.

2.7 On the standard deviations in the prediction of the Treloar data

To compare the predictive capability of the composite model and of the eight-chain model, we need to evaluate the error in the prediction by the composite model of the Treloar experimental data. This section deals with the search for the parameters of the composite model, and subsequently the calculation of standard deviations.

Recalling the argument from the previous section about the partition into the areas of dominance between the stress due to the Poisson's ratio approach and the stress due to the filament theory, Young's modulus can be determined on the basis of the least squares best fit for the stretches from the region of $1.0 \leq \lambda \leq 2.0$:

$$E = 1.0038 \text{ MPa.}$$  (2.28)
Figures 2.31 and 2.32 reproduce the engineering stress due to the Poisson's ratio approach with given material constant (2.28).

![Figure 2.31](image)

**Figure 2.31**: The prediction of the engineering stress by the composite model (2.18) in the area of low uniaxial strain versus the Treloar experimental data (●).

![Figure 2.32](image)

**Figure 2.32**: The prediction of the engineering stress by the composite model (2.18) in the area of low equibiaxial strain versus the Treloar experimental data (●).

Two other parameters, the filament modulus and the maximum extensibility, were determined in the similar manner to that (2.19)-(2.24) of the section 2.5.

The choice of the \( e_{\text{max}} \) value in the minimum of the standard deviation in uniaxial test (Figure 2.33) gives the standard deviation of 4.695\% in equibiaxial experiment. The value of \( e_{\text{max}} \) in the minimum of the standard deviation in equibiaxial strain (Figure 2.34) would lead to the standard deviation of 24.001\% in uniaxial deformation.
Figure 2.33: The standard deviation in the prediction by the composite model (2.18) of the engineering stress from the Treloar experimental data in uniaxial extension.

Figure 2.34: The standard deviation in the prediction by the composite model (2.18) of the engineering stress from the Treloar experimental data in equibiaxial extension.

Therefore, we present the value of the limit to extensibility and filament modulus,

\[ e_{\text{max}} = 4.1012, \]

\[ E_f = 0.2520 \text{ MPa}, \]  

which give the least standard deviation we encountered in uniaxial and equibiaxial tests collectively (Figure 2.35). In fact, this curve is very similar to that in uniaxial extension only (Figure 2.33).

The standard deviation in the prediction of the Treloar uniaxial data (Figure 2.36) constitutes only 5.778%, and for the Treloar equibiaxial data (Figure 2.37) it amounts
Figure 2.35: The standard deviation in the prediction by the composite model (2.18) of the engineering stress from the Treloar experimental data in uniaxial and equi-axial extensions collectively.

just to 4.031%.

Thus, for set of parameters listed by (2.28)–(2.29) the observed agreement of the composite model with the Treloar experimental data is better than it is with the eight-chain model. It is quite encouraging but not surprising since the composite model requires one material constant more than the eight-chain model does.

Nevertheless, this suggests along with the results of two previous sections that it is advisable from the practical standpoint to exploit the composite model in the study into the mechanical behaviour of PVC.

The next chapter extends our consideration onto the yield stress of oriented PVC material, whose expression is based on the filament theory presented in the current chapter, and thus is related to the composite model in focus.
Figure 2.36: The prediction of the engineering stress by the composite model (2.18) in uniaxial extension versus the Treloar experimental data (●). (S.D.=5.778%).
Figure 2.37: The prediction of the engineering stress by the composite model (2.18) in equibiaxial extension versus the Treloar experimental data (●). (S.D.=4.031%.)
Chapter 3

The yield stress of oriented PVC and its prediction

An application of the filament model described in the previous chapter to the prediction of the yield stress is quite a logical continuation of our study on the mechanical behaviour of PVC material, and it is presented in the second section. Also we report our experimental results obtained for the yield stress of PVC sheets oriented in pure shear deformation. These results are then theoretically predicted on the basis of the filament model for the yield stress of oriented material. Simple filament model relations, applied to predict the yield stress of oriented materials, give very reasonable agreement with the experiment.

3.1 Introduction

It is shown in the previous chapter that the composite model copes very well with both sets of the available experimental data due to Kawabata and due to Treloar. Furthermore, it gives the lesser standard deviation (chapter 2, section 2.7) for the Treloar experimental data than the eight-chain model does (chapter 1, section 1.4).

Thus, it is entirely natural to extend our evaluation of the composite model onto the prediction of the yield stress of oriented material (in particular, PVC).
We base the model for the yield stress of oriented material on the filament theory. The orientation gives rise to enhanced mechanical properties. Hence, the yield stress increases in the direction of the orientation. It is incorporated by means of a filament tension, which is frozen in the material as a residual stress on cooling.

Our experimental study on the yield stress of PVC material oriented in pure shear covers samples cut at different angles to the unstretched side of the sheet: \( \varphi = 0^\circ, 30^\circ, 60^\circ, 90^\circ \). Hence, the anisotropy is once again confirmed and characterised.

The last section of this chapter deals with the prediction of the yield stress. The interesting trends are observed.

### 3.2 The filament model for the yield stress of oriented material

To predict the yield stress of an oriented material we need to take into account the material anisotropy resulting from the prior hot-working while orienting the sample. It is assumed that before the material can yield it is first necessary to counteract the residual stress, and that additional stresses over and above this value will be required in order to produce yielding.

Therefore, if the initial yield stress of an unoriented material is equal to \( Y \), then after the orientation takes place the yield will differ in different directions, and the principal yield stresses are

\[
Y_1 = Y + \sigma'_{1f}, \\
Y_2 = Y + \sigma'_{2f}, \\
Y_3 = Y + \sigma'_{3f},
\]

(3.1)

where \( \sigma'_{1f}, \sigma'_{2f}, \sigma'_{3f} \) are the filament principal deviatoric stresses. These represent the residual stresses, which were "frozen in" on cooling below \( T_g \) during orientation.
process and thus are required to overcome first in order to produce yielding then. Principal deviatoric stresses may be written as
\[
\sigma'_{1f} = \sigma_{1f} - \frac{1}{3} (\sigma_{1f} + \sigma_{2f} + \sigma_{3f}), \\
\sigma'_{2f} = \sigma_{2f} - \frac{1}{3} (\sigma_{1f} + \sigma_{2f} + \sigma_{3f}), \\
\sigma'_{3f} = \sigma_{3f} - \frac{1}{3} (\sigma_{1f} + \sigma_{2f} + \sigma_{3f}).
\]
(3.2)

Note that there is the difference with the expressions for the filament stresses (2.16)
\[
\sigma_{1f} = \lambda_1 \cos \alpha_1 (t_f + t_p), \\
\sigma_{2f} = \lambda_2 \cos \alpha_2 (t_f + t_p), \\
\sigma_{3f} = \lambda_3 \cos \alpha_3 (t_f + t_p),
\]
(3.3)
in accounting the pre-stress \( t_p \), which could arise due to orientations during the initial moulding, disorientations during the annealing period, and recovery between drawing and testing; \( \lambda_1, \lambda_2, \lambda_3 \) correspond to the extension ratios during the orientation and all the other variables have the same meaning as these do in the previous chapter.

Now to predict the yield stress in the \( X_1 \)-direction resulting from the turn of the \( x_1 \)-axis counterclockwise on the \( \theta \)-angle
\[
X_1 = x_1 \cos \theta + x_2 \sin \theta, \\
X_2 = -x_1 \sin \theta + x_2 \cos \theta, \\
X_3 = x_3,
\]
(3.4)
we need to transform the yield stress tensor of the second rank
\[
Y_{X_1,X_1} = Y_1 \frac{\partial x_1}{\partial X_1} \cdot \frac{\partial x_1}{\partial X_1} + Y_2 \frac{\partial x_2}{\partial X_1} \cdot \frac{\partial x_2}{\partial X_1} + Y_3 \frac{\partial x_3}{\partial X_1} \cdot \frac{\partial x_3}{\partial X_1}.
\]
(3.5)
On the basis of (3.4) and (3.5) the yield stress in the \( \theta \)-direction may be expressed as
\[
Y_\theta = Y_1 \cos^2 \theta + Y_2 \sin^2 \theta.
\]
(3.6)

In the next section we present the experimental data on the yield stress of oriented PVC material and give the description of the tests performed.
3.3 The experimental data on the yield stress of oriented PVC

In the previous chapters we based our evaluation on the experimental data due to Treloar and the extensive experimental data due to Kawabata. To evaluate the predictive ability of the filament model for the yield stress of oriented PVC we perform our own set of experiments from sample preparations to the tensile tests.

Before proceeding to the experimental data itself, we describe our tests. First, we performed the orientation of a PVC sheet with thickness of 1.0 mm. The dimensions of the initial sheet is presented in Figure 3.1. A PVC sheet has been stretched at

![Figure 3.1: Square sample for the unidirectional orientation.](image)

temperatures \( \geq 90^\circ C \) and at a draw rate of 50 mm/min in the draw direction, and then allowed to cool to room temperature whilst being held in the stretched state. No annealing process took place.
PVC material was oriented in one direction but not uniaxially: the type of deformation was a pure shear, which is a pure homogeneous strain in which one of the principal extension ratios is 1.0 and the volume is preserved,

\[ \lambda_1 = 1, \quad \lambda_2 = \lambda_p, \quad \lambda_3 = 1/\lambda_p. \]  

(3.7)

It can be produced by stretching a sheet of PVC in such a way that its width remains unchanged.

We obtained a close approximation to a pure shear by simply stretching a short wide strip (100 mm x 10 mm) of the PVC sheet (Figure 3.2) clamped along the edge CD and gripped at nodes A and B. The length was large in comparison to the width, and thus the non-uniformity of strain is relatively slight, and is limited to a small outer region. This is illustrated in Figure 3.2, representing the appearance of equally spaced vertical lines in a strip of the PVC sheet of "length" 100.0 mm and "width" about 10 mm.

Figure 3.2: A single strip of the sample oriented in a pure shear.

Pure shear deformation is more closely related to uniaxial extension than to equibiaxial one because chain stretch occurs due to stretching along one principal direction with chains being drawn from one direction transverse to the extension direction in pure shear. Thus a pure shear experiment yields a limiting stretch value which is
similar to that in uniaxial extension. The comparison of biaxial, uniaxial, and pure shear deformations has been given in section 1.4.

Table 3.1 gives the forces necessary to stretch the PVC sheet up to the required extension ratio at the temperature about $T = 93\, ^\circ C$. The initial area over which the engineering stresses acted was $120.0 \, \text{mm} \times 1.0 \, \text{mm} = 1.2 \cdot 10^{-4} \, \text{m}^2$.

Afterwards we cut a number of samples at the different angles ($\varphi = 0^\circ$, $30^\circ$, $60^\circ$, $90^\circ$) to the unstretched direction to produce the standard dumbbell (Figure 3.3) for the tensile test.

<table>
<thead>
<tr>
<th>Pure shear, $\lambda_p$</th>
<th>Number of tests</th>
<th>Force (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>4</td>
<td>546.75</td>
</tr>
<tr>
<td>2.0</td>
<td>4</td>
<td>711.00</td>
</tr>
<tr>
<td>2.5</td>
<td>3</td>
<td>923.00</td>
</tr>
<tr>
<td>3.0</td>
<td>2</td>
<td>1080.00</td>
</tr>
</tbody>
</table>

Table 3.1: Forces required to bring the stretches up to the necessary value.

Figure 3.3: The standard dumbbell prepared for the tensile test.
<table>
<thead>
<tr>
<th>Angle, $\varphi$</th>
<th>Pre-stretch, $\lambda_p$</th>
<th>Number of tests</th>
<th>Yield (MPa) averaged</th>
<th>Extension (mm) averaged at yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>any</td>
<td>1.0</td>
<td>10</td>
<td>73.67</td>
<td>2.170</td>
</tr>
<tr>
<td>90°</td>
<td>1.5</td>
<td>9</td>
<td>72.05</td>
<td>1.849</td>
</tr>
<tr>
<td></td>
<td>2.1</td>
<td>8</td>
<td>84.28</td>
<td>1.908</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>6</td>
<td>91.87</td>
<td>2.164</td>
</tr>
<tr>
<td></td>
<td>3.3</td>
<td>8</td>
<td>103.88</td>
<td>1.869</td>
</tr>
<tr>
<td>60°</td>
<td>1.5</td>
<td>4</td>
<td>68.10</td>
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<td></td>
<td>1.6</td>
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Table 3.2: Our experimental data on the yield stress in different directions for PVC material oriented in pure shear. The angle is measured counterclockwise from the unstretched axis.
A more detailed account of experimental arrangements and the equipment used can be found elsewhere [9, 10, 12, 13].

Our experimental data on the yield stress of oriented PVC in different directions is presented in the Table 3.2. The number of tests for different pre-stretches are scattered because an actual extension ratio of a pre-stretch measured locally for a standard dumbbell (Figure 3.3) differs from an extension ratio ($\lambda_p = 1.5, 2.0, 2.5, 3.0$) applied to pre-stretch a whole sheet.

It is interesting to point out that the extension ratio at yield (Table 3.2) is almost uniform and it varies within the narrow range

$$1.05792 \leq \lambda_y \leq 1.0868,$$

where the subscript $y$ refers to the point of yield. In fact, its low value suggests that the elastic stress is insignificant in the observed yielding.

The Table (3.2) also shows how anisotropic PVC material became after the orientation took place. The values of the yield stress in different directions are scattered significantly.

In the next section we predict the yield stresses for oriented PVC reported in the current section. Also we evaluate standard deviations in those predictions.

### 3.4 Prediction of the yield stress of oriented PVC

In the last section of this chapter we deal with prediction of our experimental results on the yield stress of PVC material oriented in pure shear and with evaluation of the standard deviations encountered in this modelling.

To model the yield stress of oriented PVC we ought to determine three physical constants of the material: the limit to extensibility $e_{\text{max}}$, the filament modulus $E_f$, and the pre-stress $t_p$. These have been chosen on the basis of the experimental data
on the yield stress (Table 3.2) in the direction $\varphi = 90^\circ$. It is the most reliable set of
data obtained, i.e. it has the highest average number of tests performed per one pre-stretch. Also the choice is partially due to almost the highest value of the pre-stretch done, that guarantees us to have the best agreement we can achieve at the maximum pre-stretch ($\lambda_p = 3.4$) corresponding to a maximum value of filament extension

$$\max_{1.0 \leq \lambda_p \leq 3.4} e = 1.0532,$$

here subscript ps indicates deformation in pure shear.

Material parameters (in particular, $E_t$ and $t_p$) have been chosen through the similar procedure to one of the section 2.5, i.e. the least squares best fit has been applied for each value of $e_{\max}$ to the deviation function (square of the S.D.)

$$D_w(E_t, t_p) = \frac{1}{\sum_{\lambda_p(\varphi)} w(\lambda_p)} \sum_{\lambda_p(\varphi)} w(\lambda_p) \frac{|Y_{\text{exp}}(\lambda_p) - Y_{\text{eq}}(\lambda_p, E_t, t_p)|^2}{Y_{\text{exp}}^2(\lambda_p)},$$

weighted with respect to the number of tests $w(\lambda_p)$ corresponding to the pre-stretch $\lambda_p = \lambda_p(\varphi)$, which are given in Table 3.2. (Note that the initial yield stress of an unoriented material equals to $Y = 73.67$ MPa.)

Figure 3.4: The standard deviation in the prediction of the yield stress by the filament theory (3.1) from our experimental data on PVC in the directions: $\varphi = 90^\circ$ (solid) and $\varphi = 0^\circ$ (dashed).

Figure 3.4 indicates that the standard deviation decreases with growth of maximum extensibility parameter for the data on samples cut at the angle $\varphi = 90^\circ$, 
whereas the standard deviation for the yield stress at angle $\varphi = 0^\circ$ calculated with the same set of parameters would, however, increase (Figure 3.4).

Nevertheless, the standard deviation in both directions remains in a reasonable range. This justifies our choice of the maximum extensibility corresponding to a minimum of the standard deviation in both tests ($\varphi = 90^\circ$ and $\varphi = 0^\circ$) collectively (Figure 3.5), but two other material parameters have still been chosen on the basis of the data for the direction $\varphi = 90^\circ$ alone.

![Figure 3.5](image)

Figure 3.5: The standard deviation in the prediction of the yield stress by the filament theory (3.1) from the experimental data on PVC in two directions: $\varphi = 90^\circ$ (solid) and $\varphi = 0^\circ$ (dashed) collectively.

Hence, the set of material constants: the limit to extensibility, the filament modulus and the pre-stress have the values

$$e_{\text{max}} = 1.3575,$$

$$E_r = 2.9598 \text{ MPa},$$

$$t_p = 6.9663 \text{ MPa}. \quad (3.9)$$

The result of fitting the yield stress in the direction $\varphi = 90^\circ$ is presented at Figure 3.6. The standard deviation is just 4.751%. The prediction of the yield stress at angle $\varphi = 0^\circ$ amounts to the standard deviation 8.755% and is shown at Figure 3.7. The high discrepancy at $\lambda_p = 1.5$ (Figure 3.7) clearly suggests that it is the error of the experiment or there is some unknown effect here, that is quite unlikely.
Figure 3.6: The prediction (solid) of the yield stress ($\bullet$) at angle $\varphi = 90^\circ$ (in the direction of pure shear orientation) for PVC oriented in pure shear. (S.D.=4.751%.)

Figure 3.7: The prediction (solid) of the yield stress ($\bullet$) at angle $\varphi = 0^\circ$ (transverse to the direction of pure shear orientation) for PVC oriented in pure shear. (S.D.=8.755%.)

Note that we measured the angle $\varphi$ to the unstretched direction. Thus, to calculate the yield stress $Y_\theta$ on the basis of (3.4)-(3.7) we need to put $Y_1 = Y_\theta$, $Y_2 = Y_{90}$, $\theta = \varphi$.

For $\varphi = 60^\circ$ the standard deviation (Figure 3.8) constitutes 7.021%. The same discrepancy at $\lambda_p = 1.5$ shows up in Figures 3.8 and 3.9 for samples cut at angle $\varphi = 60^\circ$ and $\varphi = 30^\circ$ as well. Though the curve (Figure 3.9) for the yield stress of oriented PVC for samples cut at $\varphi = 30^\circ$ is higher than the experimental data within the whole range of pre-stretches, the standard deviation is equal to only 6.395%. On the whole the errors in the prediction of the yield stress in different directions for
Figure 3.8: The prediction (solid) of the yield stress (●) at angle $\varphi = 60^\circ$ for PVC oriented in pure shear. (S.D.=7.021%).

Figure 3.9: The prediction (solid) of the yield stress (●) at angle $\varphi = 30^\circ$ for PVC oriented in pure shear. (S.D.=6.395%).

PVC material oriented in pure shear are not excessive and acceptable.

It is clear that there are two trends: one in the direction of $\varphi = 90^\circ$ and the other in the direction of $\varphi = 0^\circ$. The latter preserves for the yield stress of samples cut at $\varphi = 30^\circ$, while the former dominates for the yield stress of samples cut at $\varphi = 60^\circ$. Therefore, it is interesting to see which one succeeds in the direction $\varphi = 45^\circ$, although we do not have any experimental data to compare with.
Figure 3.10: The prediction (solid) of the yield stress at angle $\varphi = 45^\circ$ for PVC oriented in pure shear.

There is a clear indication that the trend in the direction $\varphi = 90^\circ$ is the dominant one (Figure 3.10). It is hardly surprising since this is the direction of orientation and thus the less we deviate from it, the more properties of PVC material are enhanced in this direction.

Figure 3.11: The prediction of the yield stress for PVC oriented in pure shear at the angles $\varphi = 90^\circ$ and $\varphi = 0^\circ$ and in biaxial extensions.
The trunk curve in Figure 3.11 represents the yield stress of the PVC material oriented equibiaxially, whereas the branches correspond to non-equibiaxial orientation. The direction in which the yield stress was calculated is indicated at the figure by underlining the extension ratio. Experimental points for the yield stress in the direction $\varphi = 90^\circ$ are presented by empty triangles, whereas those in the direction $\varphi = 0^\circ$ appear as filled triangles. The variations in the yield stress in Figure 3.11 reproduces the trend for the failure strength measured by M. Gilbert et al. [10].

By and large the composite model copes very well with all experimental results we used herein: extensive data due to Kawabata on isoprene rubber vulcanisate, data due to Treloar on the vulcanised 8% Sulphur rubber stretched largely, and our experimental data on the yield stress of PVC material oriented in pure shear.

Therefore, from our experience we advise the use of the composite model in the further study on the mechanical behaviour of PVC.

*We suggest that further research on tensile properties of PVC material is likely to reveal additional advantages of the composite model and thus contribute to our understanding of the mechanical behaviour of PVC in particular and of rubberlike materials in general.*
Bibliography


