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Constitutive modelling of a polymeric material subjected to chemical exposure

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Abstract

Important effects resulting from chemical exposure of a polymeric material are the alterations in its stress–strain response, its sensitivity to strain-rate effects and the development of irreversible strains. The paper presents the results of experiments conducted on membranes subjected to chemical exposure and discusses the development of a single constitutive model that is applicable to both untreated and chemically-treated materials. The constitutive modelling of both categories of polymeric materials takes into consideration the influence of large strains, strain-rate effects and irreversible effects.

Keywords: B. Polymeric material; B. Constitutive behaviour; B. Finite strain; C. Mechanical testing

1. Introduction

Synthetic materials comprising of poly-vinyl-chlorides (or PVCs) have extensive engineering applications. The motivation for this study stems from the use of PVC membranes as components of engineered barriers used to prevent migration of contaminants and other hazardous substances from landfill and other waste repositories (Koerner, 1994).

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In recent years, the use of PVC membranes or geosynthetics has been extensively promoted in geoenvironmental applications although their long-term reliability is not well understood. In particular, the interaction between a chemical and a geosynthetic material can lead to the alteration of the chemical structure of the geosynthetic, which can influence the constitutive response of the membrane. Such alterations can also adversely affect the functional requirements, particularly in terms of the loss of flexibility. Other factors including heat, ultra-violet light, high-energy radiations, ultrasonic waves, other mechanical treatments, electrical discharges, oxidation, and ozonization can also influence their mechanical behaviour. It is generally recognized that while the chemical changes associated with the modification of the polymer molecules can be marginal, they can give rise to major changes in the macroscopic mechanical properties of such materials (Tobolsky, 1960; Jellinek, 1978; Kelen, 1983). Specifically in relation to geosynthetic membranes, studies conducted by Haedrich (1995) indicate that exposure of PVCs to chemicals such as acetone results in their embrittlement, leading to a severe loss in the capacity of the material to experience large strains and its increased susceptibility to cracking and fracture. The objective of this research is to develop an approach for modelling the constitutive response of a polymeric membrane in its untreated and chemically-treated conditions.

As with rubber-like elastic materials, a characteristic feature of PVC is its ability to undergo large strains. This is attributed to its randomly oriented inter-tangled polymer chain network structure. Approaches to modelling the mechanical behaviour of elastic materials through consideration of the polymer network structure and associated kinetic theories are given by a number of investigators including Wall (1942), Treloar (1943, 1975), Flory (1969), Edwards (1971), Deam and Edwards (1976), Flory and Erman (1982), Erman and Flory (1982), Doi and Edwards (1987) and Boyd and Philips (1993). More recently, Boyce et al. (1988), Arruda et al. (1995), Sweeney and Ward (1995), Bergström and Boyce (1998), Boyce and Arruda (2000), Makradi et al. (2005), and Gurtin and Anand (2005) have also re-examined the kinetic theories and network modelling as applied to constitutive modelling of rubber-like materials that undergo substantially large strains. The phenomenological theories of hyperelastic materials, which we will incorporate into the development of a constitutive model for the PVC material, have been extensively studied in the classical works of Rivlin, Green, Adkins and others, and extensive reviews of the subject are due to Doyle and Ericksen (1956), Rivlin (1960) (see also Barenblatt and Joseph, 1997), Adkins (1961), Spencer (1970), Truesdell and Noll (1992), Hayes (2001), Selvadurai (2002) and in the volumes by Green and Adkins (1970), Ogden (1984), Lur'e (1990), Drozdov (1996), Dorfmann and Muhr (1999), Fu and Ogden (2001), Besdo et al. (2001), and Busfield and Muhr (2003). In contrast to hyperelastic pure rubber-like materials that have imperceptible irreversible phenomena in terms of permanent deformations and minimal energy dissipation during cycles of loading, PVC materials can exhibit appreciable irreversible effects resulting in the development of permanent strains during loading–unloading cycles and strain-rate effects. Most importantly, such effects can materialize even at moderately large strain levels. The development of constitutive relationships that describe the mechanical behaviour of the PVC materials therefore has to address three aspects: influence of large strains, development of irreversible strains during applications of a loading–unloading cycle and strain-rate effects. The second aspect of this research integrates the influence of prolonged chemical exposure of the PVC on the alteration of its constitutive response. The methodology adopted in the study is mainly phenomenological, since the assessment of the influences of chemical exposure on the alterations in the polymer chain network will require considerably more information on both the detailed thermo-chemical processes and the manner in which such thermo-chemical reactions can be accurately incorporated within the framework of a kinetic theory. Any such developments should also address, simultaneously, material alterations leading to embrittlement and the transformation of the polymer material to one that exhibits a pronounced yield and strain-rate effects at moderately large strains.

The paper presents results of experimental investigations of isothermal, quasi-static uniaxial tests that were conducted on samples of a PVC polymer material in their intact condition and loaded at different strain-rates. These studies are extended to include isothermal, quasi-static uniaxial tests performed on samples of the PVC polymer that have been immersed in pure ethanol, for periods ranging from 1 *week* to 9 *months*. The development of a phenomenological constitutive model for characterizing the mechanical behaviour observed in these experiments can be approached via the consideration of either a nonlinear viscoelasticity approach or a nonlinear elasticity approach that is modified to account for rate-dependency effects. The former approach is a viable one and has been developed and applied to a variety of problems involving rate-sensitive materials undergoing large strains (Rivlin, 1965; Christensen, 1971; Pipkin, 1972; Findley et al., 1976; Betten, 2002). The latter approach is simpler and has been applied by Sweeney and Ward (1995), Septanika and Ernst (1998a,b) and Amin et al. (2002) to examine the time-dependent behaviour of elastomers. We show that the latter group of constitutive models can be adopted and extended with the aid of the model proposed by Boyce et al. (1988) to develop plausible constitutive models for the PVC material in both its intact and chemically exposed states.

2. Experimental investigations

The PVC material used in the experimental investigations can be classified as a glassy polymer, thermo-plastic material with the chemical formula $(CH_2 \cdot CHCl)_n$, where n is the number of the repeating unit. Its basic structure is a randomly oriented, inter-tangled molecular chain network. The general importance of the molecular network to the deformation of polymers, resulting from molecular orientation, has been discussed in articles dealing with kinetic theories and has also been established through spectroscopic techniques (Padibjo and Ward, 1983). The mechanical, physical and chemical properties of a PVC polymer material are influenced by temperature. The glassy polymer behaviour is restricted to temperatures lower than the glass transition temperature T_g. Sweeney and Ward (1995) observed that there were distinct differences in the mechanical behaviour within glass transition range and that at a higher temperature. At a temperature below T_g, there is yield-type behaviour, which manifests itself as a higher initial slope in the uniaxial stress–strain curve followed by a rapid change to a reduced slope; this effect, however, is absent at a higher temperature. Different constitutive models therefore *seem* to be necessary to investigate the mechanical behaviour at these temperature ranges. It is known (Elicegui et al., 1997; Pita et al., 2002) that the presence of plasticizer can modify the mechanical behaviour of the PVC material at room temperature. The glass transition temperature of the PVC can be markedly lowered by plasticizers (Gumargalieva et al., 1996; Dubault et al., 2003). The mechanical behaviour of the plasticized PVC is similar to that of the unplasticized PVC at temperatures above T_g. The loss of the plasticizer can therefore lead to alterations in the mechanical behaviour of the PVC material (Shin et al., 2002; Yu and Selvadurai, 2005), including an increase in the initial modulus and the development of a noticeable yield point in the stress–strain response.

2.1. Uniaxial tests on intact PVC material

Experiments were conducted on PVC sheets of thickness 0.50 mm in their supplied condition. The effective dimensions of the specimens used in uniaxial tension tests were 50 mm in length and 25.4 mm in width. Extra material was provided at the ends of the specimen to accommodate for specially fabricated rigid grips used to hold the specimen without slippage or damage at the ends. The extra material was glued using a non-reactive instant adhesive. Ideally there is the possibility of a reaction between constituents of the adhesive and the PVC material, particularly over long periods of contact. Due to the relatively short duration of the uniaxial tests, the influence of the reactive effects of the adhesive on the mechanical behaviour of the end regions can be neglected. Further details of the experimental procedure are given by Yu and Selvadurai (2005). The specially fabricated steel grips were such that the test specimen could be stretched without development of either an eccentricity or a tilt. The narrow strip specimen has cross-sectional dimensions of 25.4 mm × 0.5 mm. The grips were mounted directly on the platforms of a servo-controlled MTS machine (Fig. 1(a)), which could be operated in a displacement control mode. (The lower set of grips was fixed and the upper part could be moved at a specified rate.) Since the specimen was highly flexible in comparison to the rigid steel grips and the testing frame, the application of a machine stiffness correction to the measured deformations was considered to be unnecessary. For relative displacements smaller than 30 mm, relative movement of the grip heads was found to be quite close to the average reading of two LVDTs located on either side of the test specimen. At larger displacements, the accuracy of the LVDTs is significantly reduced. For simplicity and accuracy, the movement of the grips is therefore taken as the change in the current gauge length l. The initial gauge length (Fig. 1(b)) is taken as $l_0 = 50$ mm. The nominal stress σ_0 is defined as the value of total load measured by the load cell divided by initial cross-sectional area of the test specimen. The strain ε_0 is calculated as the percentage change in the *initial* gauge length. All experiments were performed at a constant uniaxial strain-rate $\dot{\varepsilon}_0$, which is defined as

$$\dot{\varepsilon}_0 = \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{l - l_0}{l_0}\right). \tag{2.1}$$

The experiments were performed in a Materials Testing Laboratory, where the room temperature was approximately 22 °C. The results of the uniaxial tests conducted on intact PVC specimens are shown in Fig. 1(c). The material exhibits creep and viscous effects in the continuous stress–strain curve. Further results, derived from data at several selected points, are shown in Fig. 2(a). The inset figures shown in Fig. 2(a) indicate that the grips, while providing no slippage at the ends, also restrict the lateral contraction that accompanies the uniaxial stretching. This violates the requirement for straining the specimen to produce a homogeneous deformation, which is desirable in most theoretical developments. To observe the extent to which the end constraints influence the development of homogeneous straining, a grid was marked on the surface of the test specimen. The strains derived by considering different original gauge lengths are presented in Fig. 2(c). Test results indicate that the effects of the fixity constraints are restricted to 6.8% of the test specimen at strains up to $\varepsilon_0 \approx 44\%$ and 2.4% for specimens experiencing large strains up to $\varepsilon_0 \approx 162\%$.

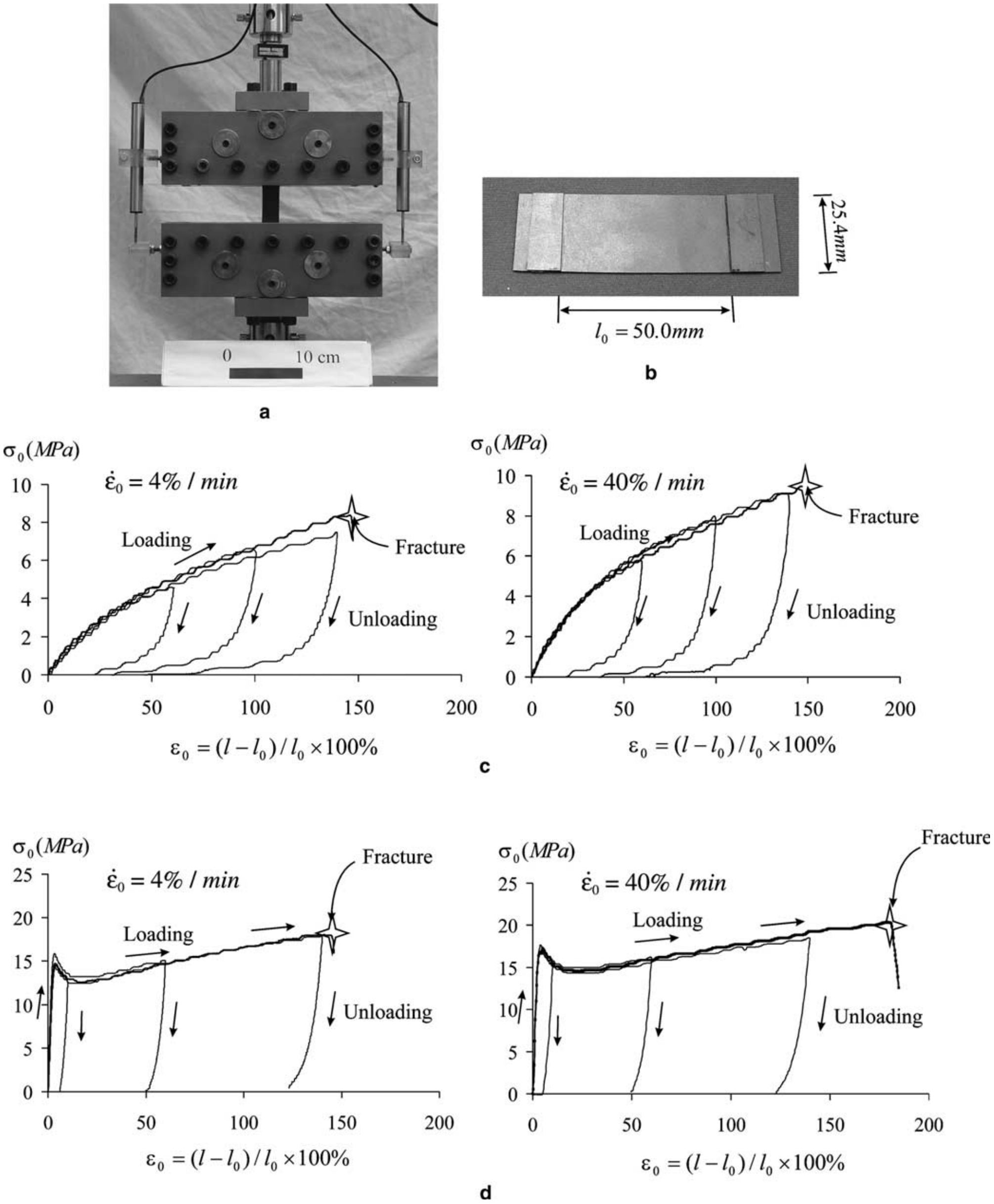

Fig. 1. Uniaxial testing on a PVC membrane: (a) experimental set-up, (b) uniaxial specimen, (c) stress–strain curves for the untreated PVC material, (d) stress–strain curves for the treated PVC material (exposed to pure ethanol for 7 *months*).

Tests were performed mainly at three different strain-rates ranging from $\dot{\varepsilon}_0 = 4\%/\text{min}$, 40%/min and 160%/min. To determine the possible influences of the machine calendering process (Penn, 1966) on anisotropy in the mechanical behaviour (Alfrey et al., 1949a),

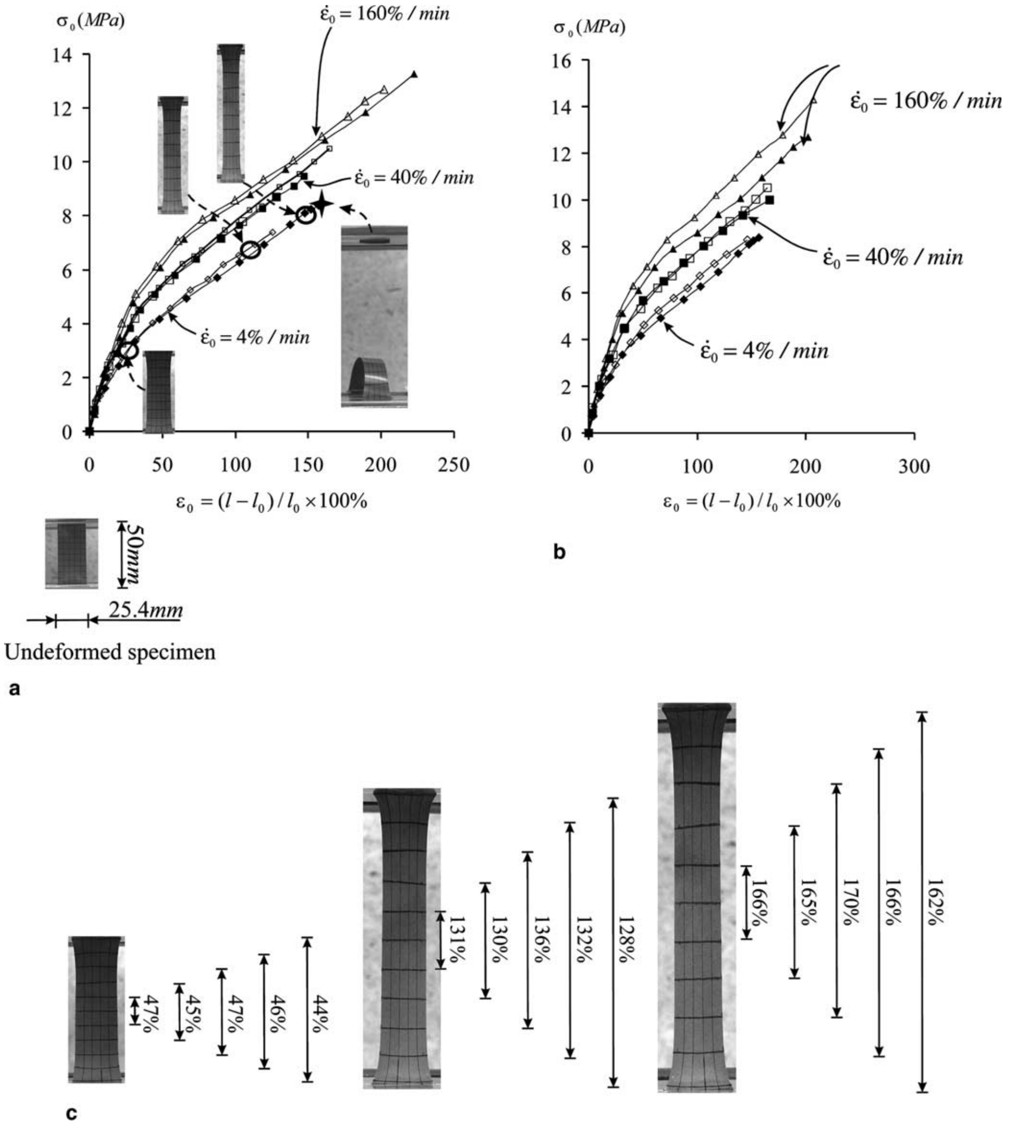

Fig. 2. Tensile behaviour of an untreated material loaded at different strain-rates: (a) repeatability of stress–strain curves, (b) isotropy of the material (filled symbols represent results tested along the machine direction and unfilled symbols represent results tested orthogonal to the machine direction), (c) deformed shapes (with strains measured at different sections of the specimen).

uniaxial tests were performed on samples, the axes of which were oriented normal to the calendering direction. Fig. 2(b) illustrates the corresponding stress–strain curves derived from uniaxial tests conducted at three strain-rates. There is evidence of the influence of the manufacturing process on the stress–strain behaviour but the results are considered to be within the range of experimental error and consequently, the influences of any manufacturing-related anisotropy are not considered in the ensuing discussions.

2.2. Uniaxial tests on PVC material subjected to chemical exposure

The PVC material used in the experimental investigations contains a plasticizer, which is classified as a *phthalate* with a chemical structure as described in Fig. 3. The objective of introducing the plasticizer is to endow the PVC with sufficient flexibility to experience large deformations without either premature yield or failure through fracture. The interaction of the PVC with chemicals can, however, lead to the leaching of the plasticizer with the attendant alterations in the constitutive behaviour. In the current research program, the PVC material was exposed to pure ethanol. The prepared test samples were immersed in ethanol ensuring that both faces of the samples were subjected to equal exposure. The longest duration of exposure was 9 *months*. Since the sample thickness is small in comparison to the area dimensions, the diffusion of the ethanol into the interior of the sample will be predominantly through-thickness. A classical diffusion analysis showed that the time required for the ethanol to achieve a 90% concentration at the central plane of the sample was approximately 0.7 *days* [based on a diffusion coefficient of $D = 1.0 \times 10^{-8}\ \mathrm{cm}^2/\mathrm{s}$ at 30 °C for a pure ethanol migration inside PVC (Messadi and Vergnaud, 1982)]. A continuous stress–strain curve for a sample subjected to a 7-*month* chemical exposure is presented in Fig. 1(d) and Fig. 4 presents the results of uniaxial tests performed on the PVC samples after different periods of exposure. These results are representative and illustrate a significant alteration in the mechanical behaviour of the PVC material due to chemical exposure. The intact material exhibits a monotonic stress–strain relationship, whereas

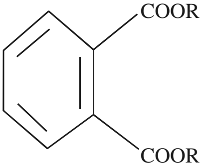

Fig. 3. Chemical structure of a phthalate plasticizer (after Wilson, 1995).

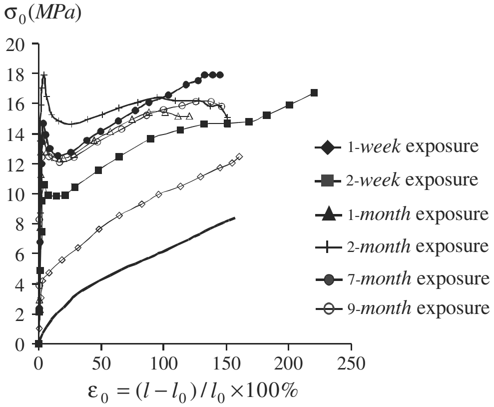

Fig. 4. Tensile behaviour of PVC material subjected to different durations of pure ethanol exposure.

Table 1
The value of $R_{O/Cl}$ for samples subjected to different periods of exposure time

Specimen	$R_{O/Cl}$ (%)
Intact PVC membrane	6.47
2-*month* exposure to pure ethanol	5.33
5-*month* exposure to pure ethanol	5.20

the samples subjected to chemical exposure exhibit embrittlement and a distinct failure threshold. Due to the leaching of the plasticizer, the yield stress of the material continuously increases up to an exposure period corresponding to 2 *months* after which there is a moderate decrease in the peak yield value, which remains unaltered by further exposure. The trends in the stress–strain responses indicate that the process of strength reduction will stabilize, although it is prudent to continue the experimentation to include several years of exposure to either a constant concentration or a constant initial concentration of ethanol. The reasons for the reduction in the "yield" stress in the stress–strain response from 2-*month* exposure to a 9-*month* exposure are not entirely clear. A likely reason is the swelling of the PVC during moisture absorption, which generally tends to reduce the strength characteristics of the material. The loss of plasticizer content was also identified through X-ray fluorescence techniques. The weight ratio of the oxygen element and chloride element in the specimen, defined by $R_{O/Cl}$, can therefore provide an indication of the plasticizer content at any stage of exposure to ethanol (Table 1). The continuous decrease in this ratio at different periods of exposure is indicative of the loss of plasticizer from the test specimen.

3. Constitutive modelling

The development of a plausible constitutive model for describing the mechanical behaviour of the PVC in its intact condition has to address the key aspects as they relate to the presence of large strains, the influence of rate effects and the occurrence of irreversible strains during a loading–unloading cycle. Similarly, the constitutive modelling of the ethanol treated PVC has to address the embrittlement process that leads to the transformation of the material from one capable of large strain hyperelastic behaviour to one that displays dominant yield behaviour, strain-rate sensitivity and associated irreversible strains. An added constraint relates to the suitability of the constitutive model for incorporation in an existing computational procedure for the study of strain-rate sensitive materials that undergo varying degrees of large strain phenomena in both the elastic and inelastic responses. As discussed, there are a variety of methodologies that can be adopted for the development of computational models for PVC materials. The purpose of the present exercise is to adopt and extend concepts that have been put forward in the literature for the modelling of both large strain elasticity phenomena, irreversible effects and to accommodate effects of strain-rate sensitivity in such responses.

The equations governing finite strain behaviour of elastic materials are presented in a number of texts and review articles on the subject (see, e.g., Rivlin, 1960; Green and Adkins, 1970; Spencer, 1970; Ogden, 1984; Lur'e, 1990) and only the essential points will be summarized. The position of a generic particle in the deformed configuration is denoted by $\mathbf{x}$ [with components x_i $(i = 1,2,3)$], the coordinates of which in the reference configuration are $\mathbf{X}$ [with components X_A $(A = 1,2,3)$]. The deformation gradient tensor is

$$\mathbf{F} = \partial\mathbf{x}/\partial\mathbf{X} \quad \text{or} \quad F_{iA} = \partial x_i/\partial X_A. \tag{3.1}$$

We can define the strain measure in terms of the tensor **B** given by

$$\mathbf{B} = \mathbf{F}\mathbf{F}^{\mathrm{T}} \quad \text{or} \quad g_{ij} = f_{iR}f_{jR} = \frac{\partial x_i}{\partial X_R}\frac{\partial x_j}{\partial X_R}. \tag{3.2}$$

The invariants of **B** are

$$I_1 = g_{ii} = \lambda_1^2 + \lambda_2^2 + \lambda_3^2, \quad I_2 = \frac{1}{\lambda_1^2} + \frac{1}{\lambda_2^2} + \frac{1}{\lambda_3^2}, \quad I_3 = \lambda_1\lambda_2\lambda_3 \tag{3.3}$$

and λ_i $(i = 1, 2, 3)$ are the principal stretches. We consider isotropic incompressible elastic materials for which $I_3 = 1$ and the Cauchy stress **T** is an isotropic function of **B** and takes the form

$$\mathbf{T} = -p\mathbf{I} + \psi_1\mathbf{B} + \psi_2\mathbf{B}^2, \tag{3.4}$$

where p is an arbitrary scalar pressure, **I** is the unit matrix and ψ_1 and ψ_2 are functions of the invariants of **B**. The constitutive equation (3.4) is a generalized relationship that can be made specific by invoking energetic/thermodynamic concepts. We assume that the incompressible hyperelastic material possesses an internal energy function W and considering energy conservation and invariance requirements applicable to an isotropic elastic material, it can be shown (Rivlin, 1960; Spencer, 1970) that in Cartesian tensor notation the generalized constitutive relationship for an incompressible elastic material undergoing finite strains can be written as follows:

$$T_{ij} = -p\delta_{ij} + 2\left[\left(\frac{\partial W}{\partial I_1} + I_1\frac{\partial W}{\partial I_2}\right)g_{ij} - g_{ik}g_{kj}\frac{\partial W}{\partial I_2}\right]. \tag{3.5}$$

The constitutive relationship (3.5) can also be made more specific through the introduction of a internal energy function with an explicit dependence on the invariants I_1 and I_2. The development of such relationships invariably relies on experimental data and the approaches adopted can range from the use of kinetic theories to phenomenological approaches. These are adequately covered in the references cited previously in connection with the modelling of rubber-like elastic materials. The most widely and successfully used phenomenological form of the internal energy function is the Mooney–Rivlin form (Mooney, 1940; Rivlin, 1948) given by

$$W(I_1, I_2) = C_1(I_1 - 3) + C_2(I_2 - 3), \tag{3.6}$$

where C_1 and C_2 are material constants. This form of the internal energy function is considered adequate for the purposes of modelling rubber-like elastic materials that are subjected to moderately large strains (Green and Adkins, 1970; Spencer, 1970). The internal energy function is also the most general form that is applicable for modelling problems in second-order elasticity theory (Rivlin, 1953; Green and Spratt, 1954; Selvadurai and Spencer, 1972; Selvadurai, 2002).

Ogden (1972) presented an alternative form of the internal energy function, which uses the principal stretches λ_1 and λ_2 as opposed to the strain invariants; i.e.,

$$W(\lambda_1, \lambda_2) = \sum_{n=1}^{N} \frac{\mu_n}{\alpha_n}\left(\lambda_1^{\alpha_n} + \lambda_2^{\alpha_n} + \lambda_1^{-\alpha_n}\lambda_2^{-\alpha_n} - 3\right) \tag{3.7}$$

with the stability constraint $\alpha_n\mu_n \geqslant 0$. It can capture the stress–strain response for an extensive range of strains encountered in highly deformable rubber-like materials. Further discussions of the internal energy functions derived through phenomenological considerations are given by Treloar (1975), Ogden (1984) and Drozdov (1996). Along the same lines, Arruda and Boyce (1993) propose the following form of the internal energy function that accommodates the 8-chain model derived from a kinetic theory:

$$W = \mu\lambda_m\left[\beta\lambda_{\text{chain}} + \lambda_m \ln\left(\frac{\beta}{\sinh\beta}\right)\right], \quad \beta = L^{-1}\left(\frac{\lambda_{\text{chain}}}{\lambda_m}\right), \quad L(\beta) = \coth\beta - \frac{1}{\beta}, \tag{3.8}$$

where μ and λ_m are, respectively, the initial shear modulus and limiting extensibility of the material such that the internal energy increases up to infinity as λ_{chain} approaches λ_m. The current chain length λ_{chain} is defined in terms of principal stretches as follows:

$$\lambda_{\text{chain}} = \left[\frac{1}{3}(\lambda_1^2 + \lambda_2^2 + \lambda_3^2)\right]^{1/2}. \tag{3.9}$$

An account of further models derived from kinetic theories is given by Boyce and Arruda (2000). Fig. 5 gives a comparison of the modelling of the tensile behaviour of the untreated PVC material for different forms of the internal energy function. The elastic parameter C_1 for the Neo–Hookean model is estimated such the model gives a reasonable fit to the experimental data up to stretch $\lambda = 1.4$. The Mooney–Rivlin form of internal energy function, however, gives a better description of the experimental data up to failure. The procedure to determine its elastic parameters C_1 and C_2 will be illustrated subsequently. Ogden's model reduces to a Neo–Hookean form when $\alpha_1 = 2$ and $N = 1$. Therefore, we choose a different value $\alpha_1 = 1.5$ for Ogden's model and the value of μ_1 is chosen such that $\mu_1/\alpha_1 = C_1 + C_2$. The parameter μ for the Arruda and Boyce's model is evaluated in a similar manner; i.e., $\mu = 2(C_1 + C_2)$. This model generally overestimates the responses; we

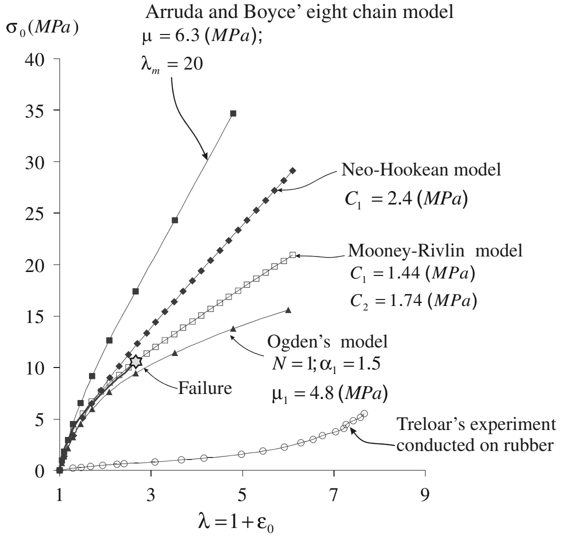

Fig. 5. Constitutive modelling of the stress–strain curve for an untreated PVC (corresponding to a loading rate of $\dot{\varepsilon}_0 = 40\%/\text{min}$) using different forms of internal energy functions.

therefore choose a sufficient large value $\lambda_m = 20$. For purposes of comparison, the experimental data on rubber obtained by Treloar (1943) are also presented. The rubber therefore is softer than a PVC material.

3.1. A model for the untreated PVC

From an inspection of the results of uniaxial tests conducted on the untreated PVC (Fig. 2(a)), it is evident that the material experiences only moderately large strains during uniaxial stretching and that the stress–strain response is sensitive to the strain-rate, particularly during the loading path. The response of the untreated PVC during unloading appears to be relatively insensitive to the loading rate (Fig. 1(c)) during a loading–unloading cycle, and the material experiences a large irreversible strain. The insensitivity of the unloading behaviour to strain-rate effects and presence of large irreversible strains after a loading–unloading cycle are also observed in experiments conducted on other polymeric material such as polyphenylene oxide (PPO) (Krempl and Khan, 2003) and polytetrafluoroethylene (Khan and Zhang, 2001). The development of a constitutive model for the untreated PVC therefore has to address the following aspects: moderately large strains and strain-rate sensitivity during stretch loading, relative insensitivity to strain-rate effects during unloading, and the development of irreversible strains during a loading–unloading cycle. This last aspect is an important consideration in the modelling of PVC as opposed to pure rubber, which experiences little or no irreversible strains during a loading–unloading cycle. A pure rubber can, however, exhibit hysteresis and the 'Mullins' effect (see, e.g., Mullins, 1947, 1969; Farris, 1971; Dorfmann and Ogden, 2004), to varying degrees, depending upon the composition of the chemicals and additives in pure rubber. The conventional theory of finite elasticity for moderately large deformations thus needs to be modified to take into consideration these additional material responses. It is highly debatable whether such a modification can be accomplished in a unique way to satisfy the mechanical behaviour of all possible polymeric materials even under the same test conditions. [The exercise is made more complicated by the presence of the plasticizer in the PVC. The polymer structure of PVC mainly consists of a head-to-tail arrangement of vinyl chloride units. The highly electro-negative nature of the chloride leads to dipoles among the polymer molecules. This in turn gives rise to a high concentration of secondary valancy forces, which contributes to the low flexibility. Plasticizers have molecules with either a polar or polarizable group, which has the capacity to bond with the polymer dipoles, thus reducing both the stiffness and the overall strength (Aiken et al., 1947; Matthews, 1996).] The objective here is to achieve the modifications through the introduction of a rate-dependent component in the definition of the internal energy function. Following the developments presented by Sweeney and Ward (1995) and Matthews et al. (1997), we assume that the internal energy function W for an incompressible PVC can be expressed in the form

$$W = W(\dot{\gamma}_0, I_1, I_2), \tag{3.10}$$

where $\dot{\gamma}_0$ is a generalized form of a combined stretch-rate that depends only on the total principal stretches λ_i, such that

$$\dot{\gamma}_0 = \frac{\mathrm{d}\gamma_0}{\mathrm{d}t}, \quad \gamma_0 = \left[(\bar{\lambda}_1 - 1)^{\frac{1}{\alpha}} + (\bar{\lambda}_2 - 1)^{\frac{1}{\alpha}} + (\bar{\lambda}_3 - 1)^{\frac{1}{\alpha}}\right]^{\alpha}, \tag{3.11}$$

where $\bar{\lambda}_i$ have a conditional dependence on λ_i to take into effect only the stretching response; i.e.,

$$\bar{\lambda}_i = \begin{cases} \lambda_i \ (\lambda_i \geqslant 1), & i = (1,2,3), \\ 1 \ (\lambda_i < 1), & i = (1,2,3) \end{cases} \tag{3.12}$$

and α is a material parameter that accounts for combined stretch. When the specimen is subjected to a uniaxial stretch, the principal stretches in other two directions are less than unity and therefore the definition of γ_0 reduces to that for the uniaxial strain ε_0. The conditional dependency indicated in (3.12) is primarily to accommodate for the observed influences of strain-rate effects when the material is subjected to stretch and the relatively marginal influence in directions where principal stretches are less than unity, especially for material that is in a form of membrane. The combined stretch γ_0 depends on the principal invariants I_1 and I_2 through (3.3), although the resulting forms are not required for purposes of parameter identification. It now remains to specify the explicit form for the internal energy function defined by (3.10). The requirement on the form of the internal energy function is that it should reduce to an appropriate finite strain equivalent in the absence of strain-rate effects. We adopt the basic functional form of the internal energy function proposed by Sweeney and Ward (1995), and select the Mooney–Rivlin form of the internal energy function as the limiting case. This latter choice is dictated by the observation that the untreated PVC material generally experiences only moderately large strains even up to failure (see also Fig. 5). The form of internal energy function corresponding to (3.10) is taken as

$$W(I_1, I_2) = C_1'(I_1 - 3) + C_2'(I_2 - 3) \tag{3.13}$$

with

$$C_1' = C_1 + \begin{cases} \kappa_1 \ln(|\dot{\gamma}_0|/\dot{\gamma}_c) & (|\dot{\gamma}_0| \geqslant \dot{\gamma}_c), \\ 0 & (|\dot{\gamma}_0| < \dot{\gamma}_c), \end{cases} \quad C_2' = C_2 + \begin{cases} \kappa_2 \ln(|\dot{\gamma}_0|/\dot{\gamma}_c) & (|\dot{\gamma}_0| \geqslant \dot{\gamma}_c), \\ 0 & (|\dot{\gamma}_0| < \dot{\gamma}_c), \end{cases} \tag{3.14}$$

where C_1' and C_2' are the modified Mooney–Rivlin parameters, κ_1 and κ_2 are parameters that define the strain-rate sensitivity and $\dot{\gamma}_c$ is defined as a *rate-independent threshold strain-rate*, below which rate-dependency is absent. The rate-dependency of the hyperelastic parameters for polymeric materials has also been observed by Gorlier et al. (2001). The constitutive postulates presented thus far are sufficient if attention is strictly focused on *monotonic loading paths* with no provision for observation of unloading behaviour, where the inelastic deformation is assumed absent and the total deformation gradient $\mathbf{F}$ coincides with the elastic deformation gradient $\mathbf{F}^e$. The loading behaviour can be studied through stretching of the uniaxial specimen up to failure at a series of loading rates $\dot{\varepsilon}_0 = 0.4\%$/min, 4%/min and 40%/min, respectively (see Fig. 6(a)). The difficulty here is to obtain the time-independent elastic responses, where experiments must be conducted at a loading rate $0 < \dot{\varepsilon}_0 = \dot{\gamma}_0 < \dot{\gamma}_c$. We therefore attempt an alternative approach for determining the rate-independent material properties through a relaxation test, where the specimen is first stretched to a certain fixed strain; then due to inelastic effects in the material, the uniaxial stress in the specimen will continuously decrease until it reaches a stable value. Examples of such relaxation tests conducted on thermoplastic polyurethanes are given by Bergström and Boyce (1998), Amin et al. (2002) and Qi and Boyce (2004). Fig. 6(a) contains plots of strains vs. stable relaxed stresses determined from relaxation tests. The internal energy function corresponding to (3.14) can be written more explicitly in relation to the elastic deformation gradient $\mathbf{F}^e$

$$W^e(I_1^e, I_2^e) = C_1'(I_1^e - 3) + C_2'(I_2^e - 3) \tag{3.15}$$

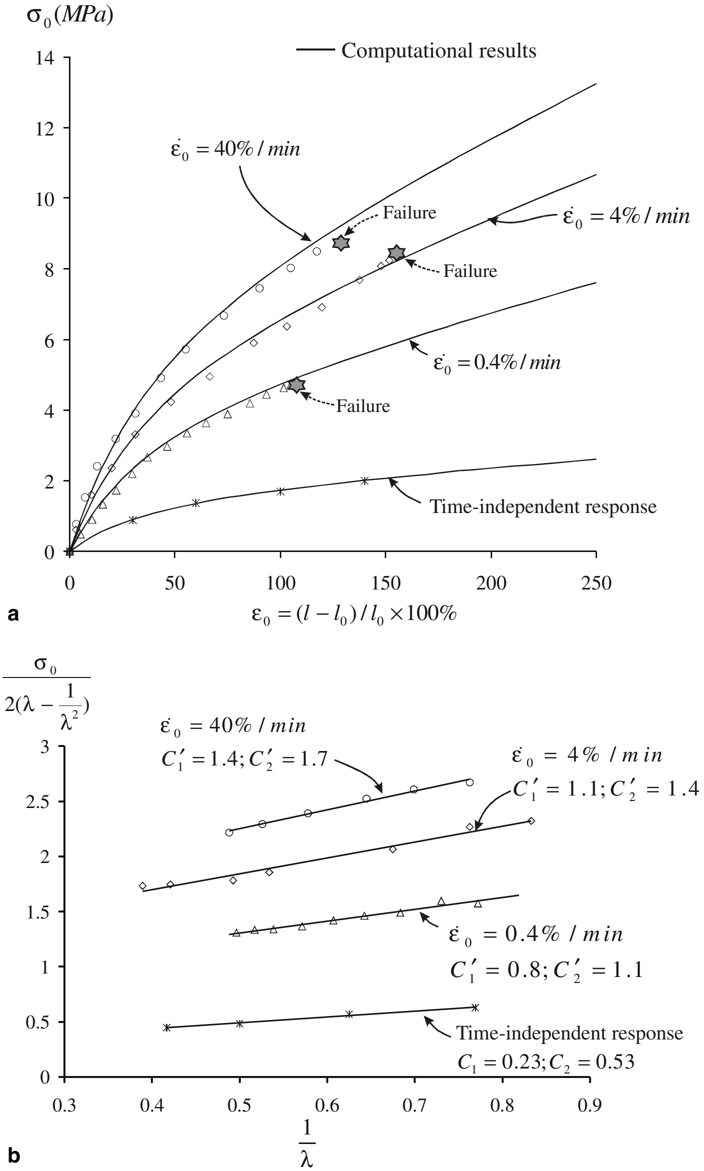

Fig. 6. Constitutive representations of the stress–strain responses for untreated PVC during monotonic loading (symbols represent experimental results): (a) test up to failure at different strain-rates, (b) determination of hyperelastic parameters ($\lambda = 1 + \varepsilon_0 \in [1.2, 2.3]$).

with the added incompressiblity constraint

$$\det \mathbf{F}^{\mathrm{e}} = 1. \tag{3.16}$$

For a particular stress–strain curve and at the stretch range $\lambda(=1+\varepsilon_0) \in [1.2, 2.3]$, the relation between $\sigma_0/[2(\lambda - 1/\lambda^2)]$ (where σ_0 is the nominal stress) and $1/\lambda$ is linear, the slope of which gives the value of C_2' and the intercept of which (as $1/\lambda \to 0$) gives the value of C_1'. The curve-fitting is performed using a least squares technique (see Fig. 6(b)) for determining C_1' and C_2' of untreated PVC at a particular loading rate. The relevant material parameters required to define C_1' and C_2' through (3.14) are given by: $C_1 \approx 0.23$ MPa; $C_2 \approx 0.53$ MPa; $\kappa_1 = \kappa_2 = \kappa \approx 0.13$; $\dot{\gamma}_c \approx 5.67 \times 10^{-7}\ \mathrm{s}^{-1}$. The model duplications of the stress–strain curves obtained by using the above set of parameters and for the three strain rates $\dot{\varepsilon}_0 = 0.4\%/\mathrm{min}$, 4%/min and 40%/min are shown in Fig. 6(a). The constraints introduced by (3.15) illustrate that an elastic deformation of the material correspond to the absence of strain-rate effects upon unloading along with complete reversal of strains. An inspection of the unloading response of the untreated PVC (Fig. 1(c)) indicates that the initial unloading modulus is significantly higher than that for the loading mode and that permanent deformation accompanies unloading behaviour. Furthermore, the permanent strains themselves are also in the moderately large strain range. In general, the mechanisms contributing to such irreversible phenomena can include both elastic and visco-plastic effects. Following these observations and assumptions, we consider additional constitutive responses, which are then added in series to the elastic constitutive component represented by the modified form of the Mooney–Rivlin internal energy function (3.15). The model can be visualized as including an elastic component A of the finite strain contributing to the elastic recovery, in parallel with a visco-plastic component B accounting for irreversible effects during unloading (Fig. 7 shows a schematic arrangement of the constitutive components). If the modelling of the finite strains during loading is accommodated through a Mooney–Rivlin model applicable to moderately large strains, then it is sufficient that the finite strain elastic recovery behaviour of the unloading response can also be modelled through the use of a internal energy function of the Mooney–Rivlin form of an elastic component A:

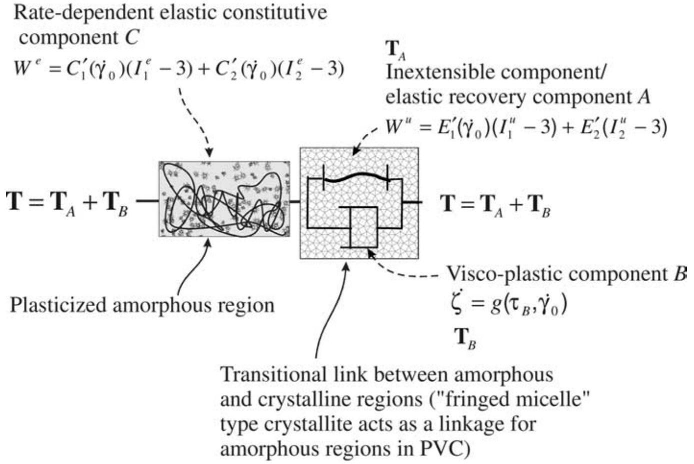

Fig. 7. Schematic representation of the constitutive components.

$$W^{\mathrm{u}}(I_1^{\mathrm{u}}, I_2^{\mathrm{u}}) = E_1'(I_1^{\mathrm{u}} - 3) + E_2'(I_2^{\mathrm{u}} - 3), \tag{3.17}$$

where E_1' has the conditional constraints

$$E_1' = \begin{cases} \to \infty & (\dot{\gamma}_0 \geqslant -\dot{\gamma}_c^{\mathrm{v}}) \\ 0 & (\dot{\gamma}_0 < -\dot{\gamma}_c^{\mathrm{v}}) \end{cases} \tag{3.18}$$

and the superscript ‘u’ signifies the unloading mode. The special treatment of E_1' is intended to take into account the fully elastic behaviour at the loading stage (i.e., $\dot{\gamma}_0 > 0$), where any development of visco-plastic deformation is restricted due to the infinite value of E_1'. We further assume that, at sufficiently low loading rates, lower than, say, a *viscous threshold strain-rate* $\dot{\gamma}_c^{\mathrm{v}}$ (i.e., $|\dot{\gamma}_0| \leqslant \dot{\gamma}_c^{\mathrm{v}}$), strain-rate effects are absent. Upon unloading (i.e., $\dot{\gamma}_0 < -\dot{\gamma}_c^{\mathrm{v}}$), however, the visco-plastic deformation is fully activated due to the zero value of E_1'. The elastic parameter E_2' is then the only remaining elastic parameter that contributes to the elastic recovery during unloading. We assume that E_2' is both time- and history-independent. It is also possible to interpret the special behaviour of modulus E_1' in terms of the transformations of the polymer chain network through a transitional link between the amorphous regions and the crystalline regions and by considering the response of such links during both loading and unloading. The inextensible transitional link can only accommodate incremental loading, but little incremental unloading. We also refer to the work of Boue et al. (1988), Jones and Marques (1990) and Drozdov and Dorfmann (2003) that deals with the concept of an inextensible strand connecting two neighbouring junctions in a polymeric material, which contributes to this response. The existence of the “fringed micelle” type crystallite that acts as a linkage for the amorphous network was experimentally confirmed by Aiken et al. (1947) and Alfrey et al. (1949a,b). Particularly, Alfrey et al. (1949b) found that the crystallites formed an oriented structure after a pre-stretch history. Therefore, we assume that due to oriented alignment between the amorphous network and the crystallite, the region in the vicinity of a connection cannot sustain any unloading immediately following a monotonic loading. The procedure adopted here, however, is mainly phenomenological with the modelling based on experimental observations.

We now focus on the modelling of the visco-plastic component B that contributes to the development of irreversible strains during unloading. A model proposed by Boyce et al. (1988), Arruda et al. (1993) and Gurtin and Anand (2005) assumes that the finite irreversible strain-rate $\mathbf{D}^{\mathrm{u}}$ is related to the deviatoric component of the effective stress tensor $\mathbf{N}_B$ associated with the visco-plastic effects through a relationship of the form

$$\mathbf{D}^{\mathrm{u}} = \dot{\zeta}\mathbf{N}_B, \quad \mathbf{N}_B = \frac{3}{2\tau_B}\mathbf{T}_B', \quad \tau_B = \left[\frac{3}{2}\mathrm{tr}\,(\mathbf{T}_B'^2)\right]^{1/2}, \tag{3.19}$$

where $\mathbf{T}_B'$ is the deviatoric component of the Cauchy stress tensor $\mathbf{T}_B$ applicable to the visco-plastic phenomena, as pictorially depicted in Fig. 7 (see also Sweeney and Ward, 1995). In general, in (3.19) the visco-plastic strain-rate $\dot{\zeta}$ is assumed to be a function of the effective stress τ_B (in MPa) and the strain-rate $\dot{\gamma}_0$, i.e.,

$$\dot{\zeta} = g(\tau_B, \dot{\gamma}_0). \tag{3.20}$$

A possible explicit form of (3.20) is a *power law relationship* either in the form

$$\dot{\zeta} = \left(\frac{\tau_B}{q}\right)^{1-s} |\dot{\gamma}_0| \begin{cases} \frac{1}{(|\dot{\gamma}_0|/\dot{\gamma}_c^{\mathrm{v}})^s} & (|\dot{\gamma}_0| \geqslant \dot{\gamma}_c^{\mathrm{v}}), \\ 1 & (|\dot{\gamma}_0| < \dot{\gamma}_c^{\mathrm{v}}) \end{cases} \tag{3.21}$$

or

$$\mathrm{d}\zeta = \left(\frac{\tau_B}{q}\right)^{1-s} |\mathrm{d}\gamma_0| \begin{cases} \frac{1}{(|\dot{\gamma}_0|/\dot{\gamma}_c^{\mathrm{v}})^s} & (|\dot{\gamma}_0| \geqslant \dot{\gamma}_c^{\mathrm{v}}), \\ 1 & (|\dot{\gamma}_0| < \dot{\gamma}_c^{\mathrm{v}}), \end{cases} \tag{3.22}$$

where q (in MPa) can be interpreted as a *static yield stress* of the material and s is the *viscous sensitivity* to rate-effects. We assume that, at sufficient low strain-rates $|\dot{\gamma}_0| \leqslant \dot{\gamma}_c^{\mathrm{v}}$, the material behaviour is rate-independent. There are two possible categories of behaviour involving rate-independency: either time-independent or time- and history-independent behaviour. The time-independent behaviour mainly manifests in the form of an *elasto-plastic* response, whereas the time- and history-independent behaviour results in a purely *elastic* response. Therefore, when the strain-rate satisfies the constraint $|\dot{\gamma}_0| < \dot{\gamma}_c^{\mathrm{v}}$, the *incremental viscous strain* $\mathrm{d}\zeta$ is independent of the time effect in spite of a possible history-dependency. Hence, in this case, *dζ* should be referred to as an *incremental plastic strain* rather than *incremental viscous strain*. Also, as s becomes small (i.e., $s \to 0$), the time-dependency of the *incremental viscous strain* $\mathrm{d}\zeta$ on $\dot{\gamma}_0/\gamma_c^{\mathrm{v}}$ is also highly restricted. Therefore, in the stress–strain responses for the tested samples conducted at $|\dot{\gamma}_0| \geqslant \dot{\gamma}_c^{\mathrm{v}}$, the rate-insensitivity of the unloading behaviour of the untreated material can be attributed to low value of s. The finite irreversible strain-rate $\mathbf{D}^{\mathrm{u}}$ is obtained by considering the product decomposition of the deformation gradient tensor into its elastic and irreversible components, as suggested by Kröner (1960) and Lee (1969) (see also, Miehe, 1994; Lubarda, 2004; Gurtin and Anand, 2005), i.e.,

$$\mathbf{F} = \mathbf{F}^{\mathrm{e}}\mathbf{F}^{\mathrm{u}}. \tag{3.23}$$

It may also be noted that the general theories of elastic plastic deformation considered by Pipkin and Rivlin (1970) and Owen (1970) also employ the product decompositions of the form (3.23) and the commutability of the representation (3.23) has also been proved by Clifton (1972). The strain-rate and irreversible strain-rate are defined (Malvern, 1969; Spencer, 2004) by

$$\mathbf{L} = \dot{\mathbf{F}}\mathbf{F}^{-1} = \mathbf{D} + \mathbf{W} = \dot{\mathbf{F}}^{\mathrm{e}}(\mathbf{F}^{\mathrm{e}})^{-1} + \mathbf{F}^{\mathrm{e}}[\dot{\mathbf{F}}^{\mathrm{u}}(\mathbf{F}^{\mathrm{u}})^{-1}](\mathbf{F}^{\mathrm{e}})^{-1}, \quad \mathbf{L}^{\mathrm{u}} = \dot{\mathbf{F}}^{\mathrm{u}}\mathbf{F}^{u^{-1}} \tag{3.24}$$

and

$$\mathbf{D}^{\mathrm{u}} = \frac{1}{2}[\mathbf{L}^{\mathrm{u}} + (\mathbf{L}^{\mathrm{u}})^{\mathrm{T}}] \tag{3.25}$$

with $\mathrm{tr}(\mathbf{D}^{\mathrm{u}}) = 0$. For example, for a uniaxially stressed element

$$D_{11}^{\mathrm{u}} = \frac{\partial \dot{x}_1^{\mathrm{u}}}{\partial x_1^{\mathrm{u}}} = \frac{\partial \dot{x}_1^{\mathrm{u}}}{\partial X_1}\frac{\partial X_1}{\partial x_1^{\mathrm{u}}} = \frac{\dot{\lambda}_1^{\mathrm{u}}}{\lambda_1^{\mathrm{u}}} = \dot{\zeta}. \tag{3.26}$$

Finally, following Boyce et al. (1988) the stress states in the elastic recovery and the visco-plastic responses applicable to the unloading paths are added to generate the Cauchy stress. Denoting the stress due to the elastic recovery response by $\mathbf{T}_A$ (see Fig. 7) and the stress due to the visco-plastic response by $\mathbf{T}_B$, we have

$$\mathbf{T} = \mathbf{T}_A + \mathbf{T}_B. \tag{3.27}$$

The results of uniaxial test data derived from the untreated PVC are first used to determine the constitutive parameters associated with the above modelling approach. Although the experiments were conducted at three different strain-rates, $\dot{\varepsilon}_0 = 4\%/\text{min}$, $\dot{\varepsilon}_0 = 40\%/\text{min}$ and $\dot{\varepsilon}_0 = 160\%/\text{min}$, only the results for two of these strain-rates ($\dot{\varepsilon}_0 = 4\%/\text{min}$, $\dot{\varepsilon}_0 = 40\%/\text{min}$ will be used to determine the material parameters and the third data set is used to assess the predictive capabilities of the parameter identification exercise. The curve fitting is carried out using the MATLAB© program.

The insensitivity of the unloading response to strain-rates essentially indicates a near-zero value of s. As discussed previously, when $s \approx 0$, the viscous model reduces to a time-independent plastic model; therefore the *viscous threshold critical strain-rate* $\dot{\gamma}_c^{\text{v}}$ is inapplicable for the untreated material. In cases where viscous effects are important, the exact non-zero value of s needs to be determined. Also, since there is no distinct yield point in the time-independent stress–strain behaviour, the *static yield stress* q also becomes irrelevant in the constitutive description of the loading response for the untreated PVC material. The parameter q, however, determines the steepness of the unloading part of the stress–strain curve at the transitional point from loading to unloading. Considering a fit to the data derived from the unloading response of the untreated material at the loading rates of $\dot{\varepsilon}_0 = 4\%/\text{min}$ and 40%/min, we obtain $q \approx 2.0$ MPa. The final parameter E_2' determines the amount of the elastic recovery. The results of the experiments give the value $E_2' \approx 0.5$ MPa. The material parameters determined can now be used to evaluate the model response for strain-rates of $\dot{\varepsilon}_0 = 4\%/\text{min}$ and 40%/min. The representations correlate well with the experimental data obtained for tests conducted up to three peak strains of 60%, 100% and 140% (Fig. 8). The predictions of the constitutive model for the stress–strain relation corresponding to a loading rate of $\dot{\varepsilon}_0 = 160\%/\text{min}$ are included in a subsequent section. As a concluding remark, we note that the assumption of incompressibility of the material was explicitly invoked in the development of the constitutive relationships for model A. The validity of this assumption was assessed by examining the lateral contraction of the membrane specimen during monotonic stretching where the total deformation gradient $\mathbf{F}$ coincided with the elastic deformation gradient $\mathbf{F}^{\text{e}}$ for the model A. The

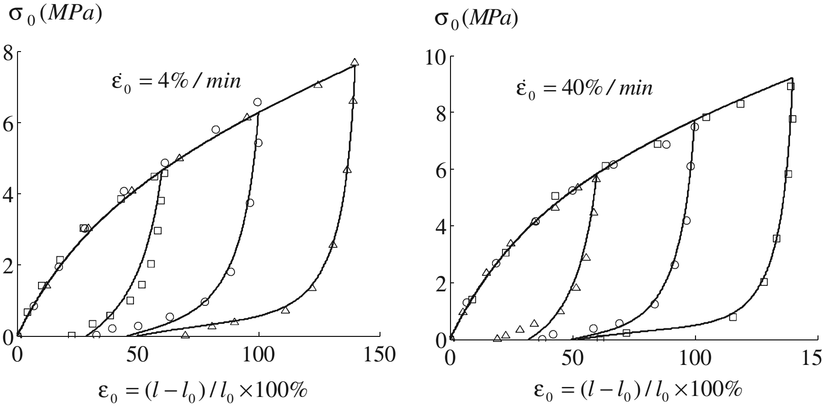

Fig. 8. Constitutive representations of the stress–strain responses involving loading and unloading for an untreated PVC (symbols represent experimental results).

results of these correlations were restricted to the region of the membrane that exhibited a near homogeneous deformation. It was found that the strain ratio gave a near incompressibility condition characterized by a third invariant with a value of approximately 0.982–0.993 (it is explicitly assumed that, during stretching, the lateral contractive strain in the thickness direction of the specimen was identical to the lateral contractive strain over the width of the specimen).

The results of uniaxial tests are insufficient to determine the parameter α. The influence of this parameter becomes appreciable particularly when the PVC material experiences a bi-axial stretching. The parameter α is estimated by conducting a uniaxial stretching of a square specimen, which is fixed along oblique directions inclined at 45° to the axis of loading (see Fig. 9). Fixity is enforced at the boundaries of the tested region using a pair of aluminium grips. As evident from the distortion of the grid marked on the test specimen, the material region experienced biaxial effects at large deformations. A computational evaluation of the experimental configuration shown in Fig. 9 was used to determine the parameter α. The correlations between the experimental results and the results of computational modelling using the software of ABAQUS/Standard (2004) that incorporated the constitutive model were performed for different values of the parameters α conducted at axial extension rates of $\dot{\eta} = 2$ mm/min and $\dot{\eta} = 20$ mm/min. At extensions $\eta > 7$ mm, the influence of the parameter α on the computational results was appreciable; the experimental response, however, becomes unreliable due to the slip between the grip and the PVC specimen. Through a comparison, the computations that used the estimated value of $\alpha \approx 3$ were able to match the experimental data at both extension rates.

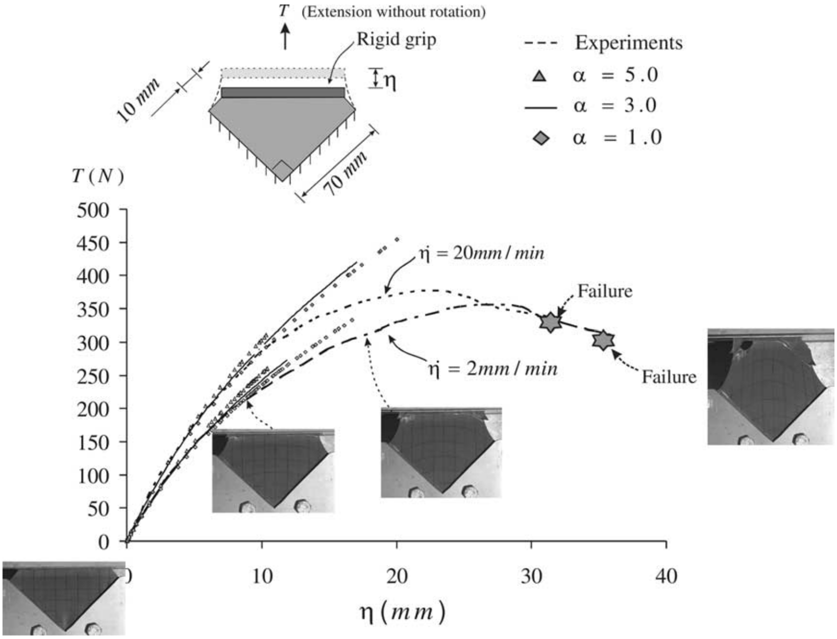

Fig. 9. Experimental determination of the material parameter α for untreated PVC.

3.2. A model for the chemically-treated PVC

The experimental investigations point to the progressive loss of elasticity of the PVC during exposure to ethanol (Fig. 4). Ideally, the development of a comprehensive model for PVC subjected to chemical exposure should address the issue of this progressive change in the mechanical behaviour, in a time-dependent fashion. A further observation is that there is a limiting mechanical response resulting from chemical exposure, beyond which continued exposure does not result in an appreciable change in the strength of the PVC. For this reason, the model development for the mechanical behaviour of the PVC focuses on the commencement of the limiting level of material strength corresponding to 7 *months* of exposure to pure ethanol. The most noticeable observation in this case is the drastic increase in the stiffness of the PVC due to chemical alterations associated with the ethanol migration and the subsequent removal of the plasticizer. The characteristic hyperelastic large strain phenomena associated with loading paths for untreated PVC completely disappear; the material develops a pronounced yield point along with both strain-softening and strain-hardening responses. Finally, the material continues to sustain appreciable post yield large strains without failure (Fig. 1(d)). The constitutive model should therefore address these specific aspects. As far as permissible, the concepts put forward for the constitutive modelling of the untreated PVC will also be adopted to define the mechanical behaviour of the ethanol-treated PVC. Admittedly, a classical Hookean isotropic incompressible elastic model without the consideration of large strain effects can adequately describe the initial elastic behaviour of the chemically-treated PVC. To conform to the description of the model for the untreated material, we adopt a Neo–Hookean form of the internal energy function, which can be derived from a Mooney–Rivlin form of internal energy function with $C_2' \approx 0$ and it reduces to the classical Hookean isotropic incompressible elastic model in cases where an infinitesimal strain measure is adopted. As with (3.15), the internal energy function for the treated material applicable to the loading range of the stress–strain curve takes the form

$$W^{\mathrm{e}}(I_1^{\mathrm{e}}, I_2^{\mathrm{e}}) = C_1'(I_1^{\mathrm{e}} - 3) \tag{3.28}$$

with

$$C_1' = C_1 + \begin{cases} \kappa_1 \ln(|\dot{\gamma}_0|/\dot{\gamma}_c) & (|\dot{\gamma}_0| \geqslant \dot{\gamma}_c), \\ 0 & (|\dot{\gamma}_0| < \dot{\gamma}_c). \end{cases} \tag{3.29}$$

The function for C_1' can also be obtained from a series of relaxation tests (the time-independent response is presented in Fig. 10(a)) and a series of loading tests at loading rates $\dot{\varepsilon}_0 = 0.4\%/\mathrm{min}$, 4%/min and 40%/min, which indicates the following set of parameters defining the strain-rate dependency: $C_1 \approx 14.2$ MPa; $\kappa_1 \approx 12.06$; $\dot{\gamma}_c \approx 5.67 \times 10^{-7}\ \mathrm{s}^{-1}$. (The experiments conducted at loading rate 0.4%/min takes an extremely long time to reach failure. The experiments corresponding to loading rate 0.4%/min were mainly conducted to examine the linear elastic modulus of the chemically-treated material, and they were terminated once the yield point was reached.) The value of *rate-independent threshold strain-rate* ($\dot{\gamma}_c$) is found to be the same for both *untreated* and *treated* materials. Also the deviation from elastic behaviour commences with the initial yield of the treated PVC. The yield strain obtained from the data corresponds to $\zeta_{\mathrm{y}} \approx 2.8\%$. This result indicates that ζ_{y} is relatively insensitive to the duration of chemical exposure. The yield point can be interpreted as that resulting from the breakage of the transitional link, which occurs at a critical

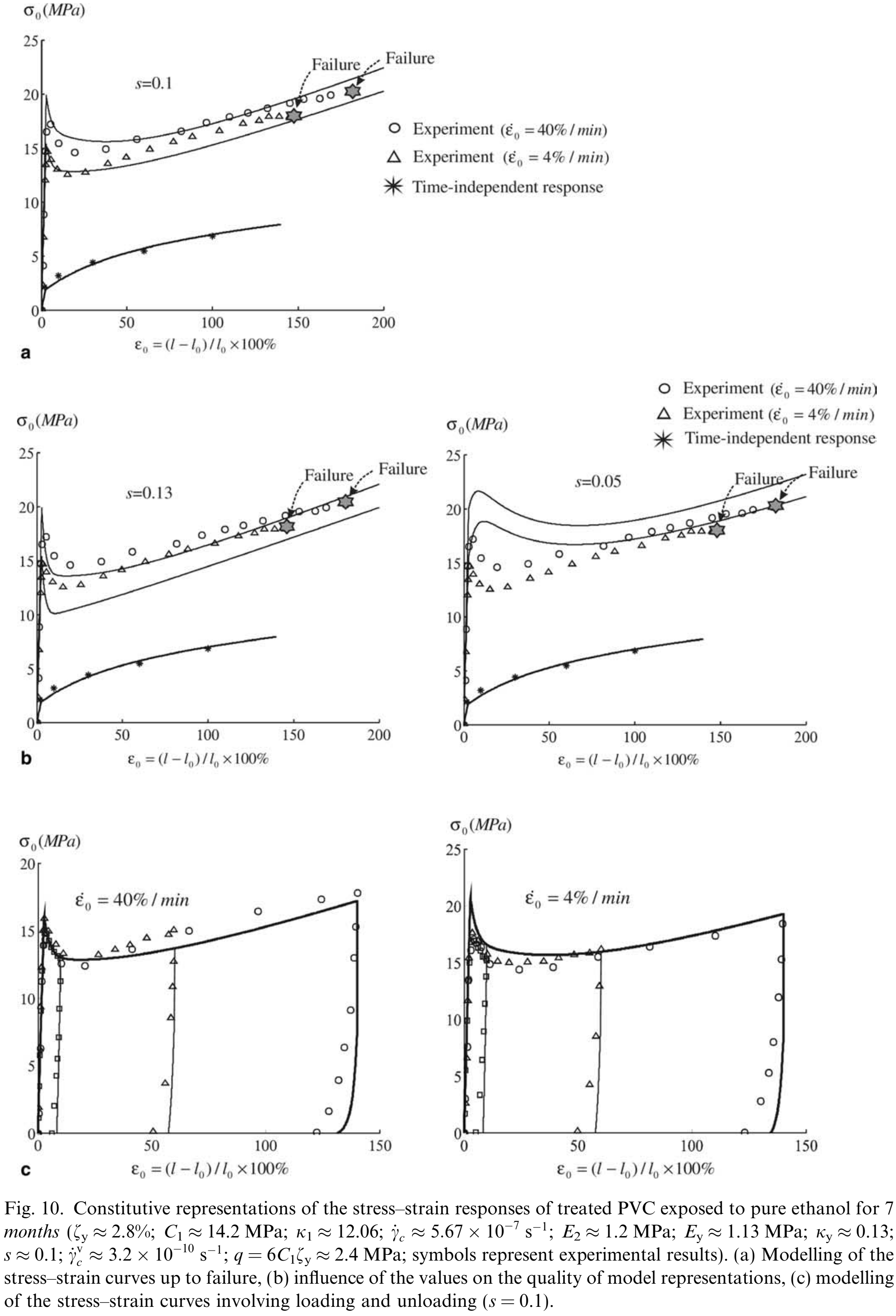

Fig. 10. Constitutive representations of the stress–strain responses of treated PVC exposed to pure ethanol for 7 *months* ($\zeta_y \approx 2.8\%$; $C_1 \approx 14.2$ MPa; $\kappa_1 \approx 12.06$; $\dot{\gamma}_c \approx 5.67 \times 10^{-7}$ s^{-1}; $E_2 \approx 1.2$ MPa; $E_y \approx 1.13$ MPa; $\kappa_y \approx 0.13$; $s \approx 0.1$; $\dot{\gamma}_c^v \approx 3.2 \times 10^{-10}$ s^{-1}; $q = 6C_1\zeta_y \approx 2.4$ MPa; symbols represent experimental results). (a) Modelling of the stress–strain curves up to failure, (b) influence of the values on the quality of model representations, (c) modelling of the stress–strain curves involving loading and unloading ($s = 0.1$).

strain $\varepsilon_0 = \gamma_0 = \zeta_y$. Its pronounced presence is then determined by the degree of susceptibility of the transitional link to the chemical exposure. The value of yield strain is, however, uninfluenced by the duration of the chemical exposure. The breakage of the transitional link is assumed to cause changes in the elasticity parameters of the elastic recovery model *A*. As with the untreated PVC, the elastic parameter E'_2 is assumed to be a constant, but E'_1 considers the yield of the material and therefore takes the form

$$E'_1 = \begin{cases} \to \infty & (\dot{\gamma}_0 \geqslant -\dot{\gamma}^{\mathrm{v}}_c \text{ and } \gamma_0 \leqslant \zeta_{\mathrm{y}}), \\ E'_{\mathrm{y}} & (\dot{\gamma}_0 \geqslant -\dot{\gamma}^{\mathrm{v}}_c \text{ and } \gamma_0 > \zeta_{\mathrm{y}}), \\ 0 & (\dot{\gamma}_0 < -\dot{\gamma}^{\mathrm{v}}_c), \end{cases} \tag{3.30}$$

where ζ_y is the yield strain and E'_y is the post-yield *hardening modulus*. The special representation for E'_1 is intended to take into account the fully elastic behaviour of the treated material prior to yield at a loading rate $\dot{\gamma}_0 \geqslant -\dot{\gamma}^{\mathrm{v}}_c$, where the visco-plastic deformation is constrained due to the infinite value assigned for E'_1. A finite value of E'_1 beyond the yield point, however, results in the development of visco-plastic deformations, which leads to a softening behaviour of the material and subsequent hardening behaviour in the large strain range (e.g., $\varepsilon_0 = 100$–150%). Upon unloading (i.e., $\dot{\gamma}_0 < -\dot{\gamma}^{\mathrm{v}}_c$), the visco-plastic deformation is fully activated due to the zero value of E'_1, which leads to appreciable irreversible visco-plastic permanent strains. The possibility of the rate-dependency of the *hardening modulus* E'_y is also considered; i.e.,

$$E'_{\mathrm{y}} = E_{\mathrm{y}} + \begin{cases} \kappa_{\mathrm{y}} \ln(\dot{\gamma}_0/\dot{\gamma}^{\mathrm{v}}_c) & (\dot{\gamma}_0 \geqslant \dot{\gamma}^{\mathrm{v}}_c), \\ 0 & (-\dot{\gamma}^{\mathrm{v}}_c \leqslant \dot{\gamma}_0 < \dot{\gamma}^{\mathrm{v}}_c), \end{cases} \tag{3.31}$$

where κ_y is the rate-sensitivity and E_y is the *rate-independent hardening modulus*. To describe the visco-plastic responses in the chemically-treated PVC, we adopt the form of either (3.21) or (3.22). Unlike with the untreated material, the visco-plastic response is not only dominant in the unloading mode, but also accounts for the softening behaviour of the material beyond the yield point ζ_y.

The parameter identification begins with an examination of the time-independent response (Fig. 10(a)). Unlike in the untreated material, there is a distinct yield point in the proposed time-independent stress–strain response. Softening behaviour is, however, absent, which proves the validity of the assumption concerning the absence of a viscous effect at limiting loading rates less than $\dot{\gamma}^{\mathrm{v}}_c$. The *static yield stress* $q(= 6C_1\zeta_y) \approx 2.4$ MPa can also be determined as a yield stress in the time-independent stress–strain curve. The values of E_y and E'_2 can be obtained by matching the *slope* of the hardening behaviour of the time-independent stress–strain curve; this gives $E_y \approx 1.1$ MPa and $E'_2 \approx 1.2$ MPa. The rate-dependency of the parameter E'_y can be obtained by matching the slope of the hardening responses for a series of loading tests conducted at the loading rates $\dot{\varepsilon}_0 = 4\%$/min and 40%/min. The relevant constitutive parameters are: $E_y \approx 1.13$ MPa; $\kappa_y \approx 0.1$; $\dot{\gamma}^{\mathrm{v}}_c \approx 3.2 \times 10^{-10}\ \mathrm{s}^{-1}$. The remaining undetermined material parameter is the *viscous sensitivity s*. When *s* is close to zero, the unloading behaviour of the material, with $E'_1 = 0$, is relatively insensitive to the loading rate. In the material softening region, where $E'_1 \neq \infty$, the rate-sensitivity is noticeable even though *s* is close to zero. Therefore, the value of *s* has a significant influence on the softening behaviour of the material where E'_1 abruptly transforms from an infinite value to a finite value E'_y beyond the yield point (i.e., $\varepsilon_0 = \zeta_y$). Fig. 10(b) shows the influence of the value of *s* on the quality of model representations. The curve fitting exercise is performed on the stress–strain curves at loading rates $\dot{\varepsilon}_0 = 4\%/\text{min}$ and 40%/min. The practice determines an appropriate estimate for $s \approx 0.1$. The parameters defining the visco-plastic response of the chemically-treated material are therefore: $q \approx 2.4$ MPa; $s \approx 0.1$; $\dot{\gamma}_c^v \approx 3.2 \times 10^{-10}\ \text{s}^{-1}$. The model representations of time-independent response and the stress–strain curves conducted up to failure at loading rates $\dot{\varepsilon}_0 = 4\%/\text{min}$ and 40%/min by material parameters derived previously are presented in Fig. 10(a). Accurate representations are obtained for the yield behaviour of the material followed by a material softening and a moderate amount of hardening at large deformations (e.g., $\varepsilon_0 = 100\text{–}150\%$). The modelling of the loading–unloading stress–strain curves at these loading rates is then presented in Fig. 10(c). The representations correlate well with the experimental data obtained for tests conducted up to three peak strains of 10%, 60% and 140%.

The procedures used in the determination of α for the untreated PVC are also used to determine the material parameter α applicable to the chemically-treated PVC. The treated PVC exposed to pure ethanol for 5 *months* followed by exposure to air for a 7-*month* period is tested with fixity enforced at boundaries inclined at 45° to the axes of loading (see Fig. 11(b)). The modelling of the uniaxial data with the material parameters derived, using a technique similar to that discussed previously for specimen exposed to pure ethanol for a period of 7 *months*, is presented in Fig. 11(a). The material parameters were further used to evaluate the computational responses of a test fixed along oblique directions at an axial extension rate of $\dot{\eta} = 2$ mm/min. The computational evaluations were performed with different values of the parameters α (Fig. 11(b)). Since the plasticizer loss appears to stabilize after 5 *month* of exposure (Table 1), it may be concluded that the material parameter α is relatively uninfluenced by the duration of chemical exposure. The material parameter $\alpha \approx 3$ is considered to be applicable to PVC specimens exposed to pure ethanol for a period of 7 *months*. The particular value of $\alpha \approx 3$ is possibly indicative of equal contributions from the three principal stretch directions of the polymeric material in the definition of $\dot{\gamma}_0$ in (3.11).

4. Predictions of the constitutive models

A *single* generalized form of a constitutive model that accounts for large strain hyperelastic behaviour, strain-rate effects and moderately large irreversible plastic strains has been developed for modelling *both* the *untreated* and *chemically-treated* PVC. The mechanical response of the *untreated* material, however, has to distinguish between loading and unloading sequences through a selective treatment of the elastic parameter of the elastic recovery component. During loading, the visco-plastic deformation of the *untreated* material is restricted and the only deformation is attributed to elastic effects; upon unloading, however, the visco-plastic component is fully activated and unloading behaviour is accompanied by irreversible deformations. For the *chemically-treated* material, the material responses additionally take into account the yield of the treated PVC. Prior to yield (as defined by a ζ_y), the visco-plastic deformation is restricted; beyond yield, however, the visco-plastic component is activated, which accounts for further softening and hardening behaviour. Tables 2 and 3 give, respectively, the summaries of the equations used for describing the general forms of the constitutive models for both the *untreated* and *chemically-treated* PVC.

The constitutive models developed in the previous section are now used to predict the uniaxial responses of the untreated and chemically-treated PVC, which are tested at the

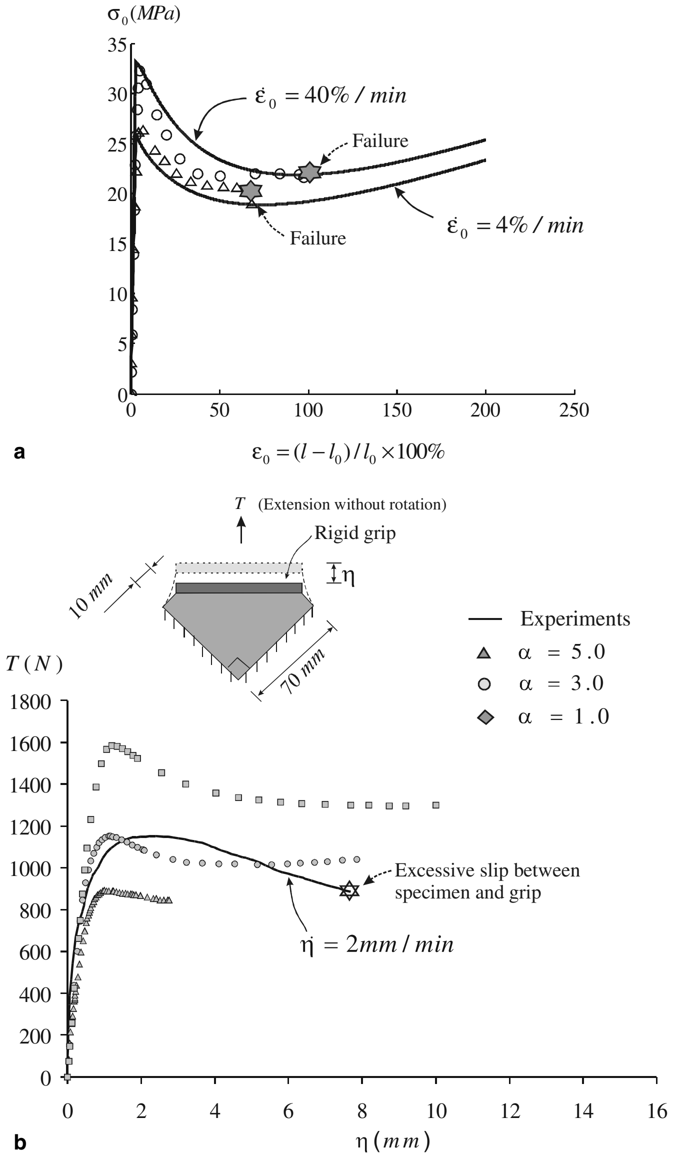

Fig. 11. Experimental determination of the material parameter α for chemically-treated PVC ($\zeta_y \approx 2.8\%$; $C_1 \approx 25$ MPa; $\kappa_1 \approx 19$; $\dot{\gamma}_c \approx 5.67 \times 10^{-7}$ s^{-1}; $E_2 \approx 1.2$ MPa; $E_y \approx 4.13$; $\kappa_y \approx 0.087$; $s \approx 0.11$; $\dot{\gamma}_c^{v} \approx 3.2 \times 10^{-10}$ s^{-1}; $q = 6\zeta_y C_1 \approx 4.13$ MPa). (a) Uniaxial behaviour (symbols represent experimental data), (b) test along oblique direction.

loading rate $\dot{\varepsilon}_0 = 160\%/$ min. The predictive capabilities of the models for a complete stress–strain curve that involves both loading and unloading have also been examined. The constitutive modelling for the treated PVC also takes into account the yield point and softening behaviour of the material. Fig. 12 shows the comparisons between the results of the model representations and the corresponding test data. The results show good

Table 2
Constitutive equations used for modelling *untreated* PVC

Components	Deformation gradient	Component A ($\mathbf{T}_A$)	Component B ($\mathbf{T}_B$)	Component C ($\mathbf{T}_C$)
Loading	$\mathbf{F} = \mathbf{F}^e$	Deformation restricted	Deformation restricted	Eqs. (3.11), (3.12), (3.14), (3.15)
Unloading	$\mathbf{F} = \mathbf{F}^e\mathbf{F}^u$	Eq. (3.17) with $E_1' = 0$	Eqs. (3.19), (3.21) or (3.22)	

Table 3
Constitutive equations used for modelling *chemically-treated* PVC

Components	Deformation gradient	Component A ($\mathbf{T}_A$)	Component B ($\mathbf{T}_B$)	Component C ($\mathbf{T}_C$)
Loading prior to yield	$\mathbf{F} = \mathbf{F}^e$	Deformation restricted	Deformation restricted	Eqs. (3.11), (3.12), (3.28) or (3.15) with $C_2' = 0$, (3.29)
Loading beyond the yield point	$\mathbf{F} = \mathbf{F}^e\mathbf{F}^u$	Eq. (3.17) with $E_1' = E_y'$ and (3.31)	Eqs. (3.19), (3.21) or (3.22)	
Unloading	$\mathbf{F} = \mathbf{F}^e\mathbf{F}^u$	Eq. (3.17) with $E_1' = 0$	Eq. (3.19), (3.21) or (3.22)	

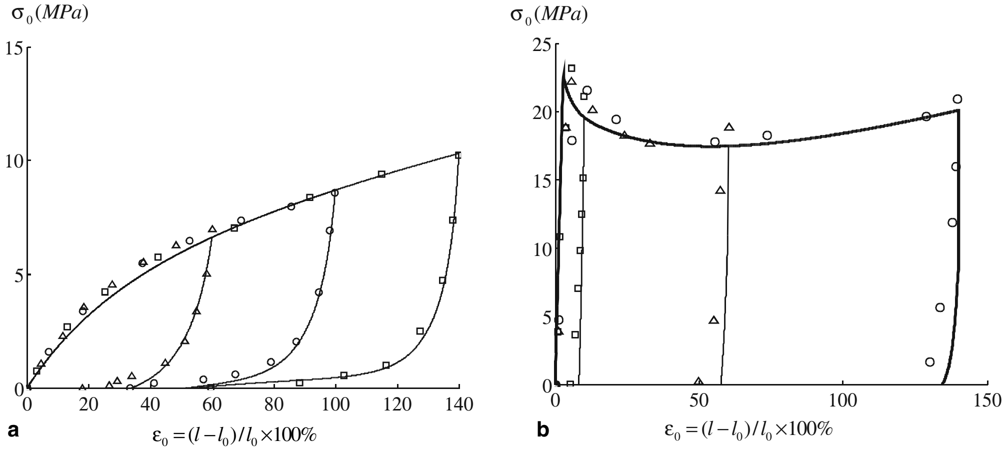

Fig. 12. Computational predictions for the stress–strain responses (corresponding to loading rate $\dot{\varepsilon}_0 = 160\%/\text{min}$; symbols represent experimental results). (a) Untreated PVC, (b) treated PVC exposed to pure ethanol for 7-months.

correlations between the two sets of results, particularly as loading–unloading cycles are carried out up to three levels of strain.

5. Concluding remarks

The accurate modelling of the mechanical response of PVC has important implications to the engineering applications of the material. The results of the experiments conducted in connection with the research program indicate that in its natural condition the PVC is only capable of undergoing moderately large strains, the finite strain response of which can be modelled by appeal to a internal energy function of the Mooney–Rivlin form. Unlike natural rubber at moderately large strains, which is virtually void of irreversible phenomena and strain-rate effects, PVC exhibits a strong rate-dependency and irreversible effects. Furthermore, the irreversible strains themselves can be within the realm of moderately large strains. The paper uses the results of a series of conventional uniaxial tests conducted on strip specimens and obliquely constrained specimens to develop a plausible constitutive model that incorporates both strain-rate effects and moderately large irreversible strains. The parameter identification is conducted using the results of two sets of strain-rates and the results of a third series of tests are used to validate the constitutive model. The calibration exercise yields highly satisfactory correlations between the predictions and the experiments, although the range of applicability of the constitutive model is strictly limited to the basic Mooney–Rivlin form of the internal energy function with the constitutive parameters that are now strain-rate dependent.

A majority of the investigations dealing with the constitutive modelling of rubber-like and highly deformable materials assume that the constitutive properties of the model remain invariant throughout the lifetime of their use. The role of chemically induced alterations in the constitutive properties of rubber-like and PVC materials is gaining attention as the impact of such alterations on the functional properties of PVC become a topic of concern. With PVC materials it is found that their interaction with chemicals such as ethanol leads to embrittlement with the attendant loss of their desirable highly elastic characteristics. The constitutive model development also addresses the loss of elasticity and the development of a distinct yield point in the stress–strain response of the chemically-treated PVC. It is shown that the basic constitutive responses involving large strain hyperelastic behaviour, strain-rate effects and moderately large irreversible plastic strains adopted for the description of the untreated PVC can also be used to describe the mechanical response of the chemically-treated PVC. Since a *single* constitutive model characterized the PVC material in its untreated and chemically-treated states, the alteration in the microstructure of the material as a result of chemical exposure can be easily examined through variations in some material parameters at different durations of chemical exposure. Although the treated PVC undergoes significant alterations in the mechanical behaviour and exhibits a distinct yield type behaviour, there is a set of material parameters, however, that are uninfluenced by the duration of chemical exposure (i.e., $\zeta_{\mathrm{y}} \approx 2.8\%$; $\dot{\gamma}_c \approx 5.67 \times 10^{-7}\ \mathrm{s}^{-1}$; $E_2 \approx 1.2$ MPa; $\dot{\gamma}_c^{\mathrm{v}} \approx 3.2 \times 10^{-10}\ \mathrm{s}^{-1}$; $\alpha \approx 3$). Here again, the constitutive model developed uses a restricted data set for parameter identification and the predictive capabilities of the model are validated using the remaining data. The correlations between the predictions of the constitutive model and the experimental data are considered to be highly satisfactory. Particularly, the constitutive model successfully characterizes the insensitivity of the unloading responses of a polymeric material to the strain-rate effects, which, to the authors' knowledge, can hardly be addressed by those based on conventional nonlinear viscoelastic model in the literature (see also Krempl, 2002; Colak, 2005).

In general, the constitutive model development for both the untreated and treated PVC results in correlations of satisfactory quality that permits the use of the models in the study of boundary value problems involving PVC membranes. The constitutive models developed are also in a sufficiently generalized form that enables their incorporation in advanced computational codes that have been developed in the literature for the modelling of membranes that can exhibit rate sensitive responses in addition to the development of moderately large elastic and irreversible plastic strains.

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Appendix A. Some thermodynamic considerations concerning the internal energy function $W(\Xi, I_1, I_2)$

The microstructure of a polymeric material experiences change during deformation as a result of either "breaking" or "forming" of the network chains (Tobolsky et al., 1944; Green and Tobolsky, 1946; Treloar, 1975). As a result, there can be corresponding alterations in the internal energy function $W(I_1, I_2, I_3)$ of the material (see Lubliner, 1985). Septanika and Ernst (1998a) proposed that the current state of the microstructure of the material could be described by an internal variable $\Xi(t)$ at time t. In the case of an incompressible material where $I_3 = 1$, the internal energy function W can be written as a function of the internal variable Ξ, i.e. (see also Lubliner, 1972; Simo, 1987; Septanika and Ernst, 1998a):

$$W = W(\Xi, I_1, I_2, S), \tag{A.1}$$

where S denotes entropy of a thermodynamic state. Although the interpretation of entropy as a state variable has been a matter of controversy (Woods, 1981, 1982), we shall assume that entropy can be accommodated through the concept of an internal variable. The first law of thermodynamics prescribes the local equation of energy balance, which can be adapted in the incremental form

$$\dot{W}(\Xi, I_1, I_2, S) = T_{ij}\dot{D}_{ij} - \nabla \cdot \vec{h} + \dot{\Psi}(\Xi, I_1, I_2), \tag{A.2}$$

where $\vec{h}$ is a vector representing heat flux; $\Psi\ (\Xi, I_1, I_2)$ denotes the contribution from other sources of permissible energy such as chemical potential, radiation or potential energy. The second law of thermodynamics can be expressed by the local expression for the Clausius–Duhem inequality:

$$\dot{S} + \nabla \cdot (\vec{h}/\vartheta) \geqslant 0, \tag{A.3}$$

where ϑ denotes the absolute temperature. Combining (A.2) and (A.3), we have (see also Lubliner, 1972; Lion, 2000)

$$\left(\vartheta - \frac{\partial W}{\partial S}\right)\dot{S} + \left(T_{ij} - \frac{\partial W}{\partial D_{ij}} + \frac{\partial \Psi}{\partial D_{ij}}\right)\dot{D}_{ij} + \left(\frac{\partial \Psi}{\partial \Xi} - \frac{\partial W}{\partial \Xi}\right)\dot{\Xi} - \frac{1}{\vartheta}\vec{h} \cdot \nabla\vartheta \geqslant 0. \tag{A.4}$$

Since $\dot{S}$, $\dot{D}_{ij}$, $\dot{\Xi}$ are arbitrarily specified, in cases where Ψ has a weak dependency on the strain invariants (i.e., $\partial\Psi/\partial D_{ij} \to 0$ or $\partial\Psi/\partial I_1 \to 0$ and $\partial\Psi/\partial I_2 \to 0$), we require that

$$\begin{aligned} \vartheta &= \frac{\partial W}{\partial S}, \\ T_{ij} &= \frac{\partial W}{\partial D_{ij}} \end{aligned} \tag{A.5}$$

and

$$\left(\frac{\partial \Psi}{\partial \Xi} - \frac{\partial W}{\partial \Xi}\right)\dot{\Xi} - \frac{1}{\vartheta}\vec{h} \cdot \nabla\vartheta \geqslant 0. \tag{A.6}$$

Since $\dot{\Xi}$ and $\nabla\vartheta$ are also independent, we require

$$\left(\frac{\partial \Psi}{\partial \Xi} - \frac{\partial W}{\partial \Xi}\right)\dot{\Xi} \geqslant 0. \tag{A.7}$$

Therefore, the second law of thermodynamics can be satisfied if there are other energy sources $\Psi(\Xi)$ such that the condition (A.7) is satisfied. A simple form of $\Psi(\Xi)$ that satisfies (A.7) can be

$$\frac{\partial \Psi}{\partial \Xi} - \frac{\partial W}{\partial \Xi} = 0 \tag{A.8}$$

which states that any change in Ψ as a result of alteration of internal variable Ξ can be transformed into the internal energy. (A.8) is sufficient to illustrate that the influence of an arbitrary history of Ξ on the internal energy is possible on the condition that there is external sources of energy. This is particularly true when stress-induced crystallization of a polymer is possible where crystallization is influenced by an internal variable such as strain-rate (Fukushima et al., 2005).

We further, however, examine a special case where $(\partial\Psi/\partial\Xi)\dot{\Xi} \to 0$. Such condition arises either when Ψ is nearly insensitive to Ξ (i.e., $\partial\Psi/\partial\Xi \to 0$) or when the variation of Ξ is relatively slow (i.e., $\dot{\Xi} \to 0$). The requirement (A.7) imposed by the second law of thermodynamics then becomes (see also Lubliner, 1972; Lubliner, 1985; Simo, 1987; Kamlah and Haupt, 1998; Huber and Tsakmakis, 2000):

$$\frac{\partial W}{\partial \Xi}\dot{\Xi} \leqslant 0. \tag{A.9}$$

The state variable Ξ can be interpreted as a damage parameter of the microstructure (Simo, 1987). In this case, the restriction (A.9) can be satisfied on condition that the material *only* experiences *damage without healing* (i.e., $\partial W/\partial\Xi \leqslant 0$ and $\dot{\Xi} \geqslant 0$). In cases where both *self-healing* and *damage* of the microstructure are possible, the evolution history of Ξ can be arbitrary; therefore, the approach to use parameter Ξ for the description of the state of the microstructure, generally does not obey the second law of thermodynamics in a first sense. This appendix addresses the possibility of an arbitrary evolution of the internal variable Ξ under the condition that $(\partial\Psi/\partial\Xi)\dot{\Xi} \to 0$.

The first fundamental assumption made here is that, for any fixed combination I_1 and I_2, W is a *continuous function* of the internal variable Ξ. As such, the dependency can, however, be either positive or negative.

Let us first consider those intervals of Ξ (say $\Xi \in [\beta_0, \beta_1]$), where $\partial W/\partial\,\Xi \geqslant 0$.

Now consider an arbitrary *continuous* evolution history $\Xi = \Xi(t)$, where t denotes the time. For those time intervals where $\dot{\Xi} < 0$, the constraint (A.9) imposed by second law of thermodynamics can be automatically satisfied. We then focus on the time intervals where $\dot{\Xi} \geqslant 0$. Following Septanika and Ernst (1998a) we can discretize the history where $\dot{\Xi} \geqslant 0$, into a series of step-intervals $t \in (t_i, t_{i+1})$, where $i = 0, 1, 2\ldots$ are integers, such that, at their transition, the slope of $\Xi = \Xi(t)$ with respect to time t vanishes (see Fig. A.1), i.e.,

$$\dot{\Xi} = 0 \quad \text{at } t = t_0, t_1 \ldots t_i. \tag{A.10}$$

At time $t \in (t_i, t_{i+1})$, however, $\dot{\Xi} \geqslant 0$. The second thermodynamic requirement (A.9) therefore prescribes that

$$\frac{\partial W}{\partial \Xi} = 0 \quad \text{at } \; t \in (t_i, t_{i+1}) \; (i = 0, 1, 2, \ldots) \tag{A.11}$$

or correspondingly,

$$W(\Xi, I_1, I_2) = \text{constant}, \quad \Xi \in (\Xi_i, \Xi_{i+1}) \; \text{ for fixed } (I_1, I_2). \tag{A.12}$$

Combining (A.10) and (A.11), the second law of thermodynamics is satisfied on the condition that

$$\frac{\partial W}{\partial \Xi}\dot{\Xi} = 0. \tag{A.13}$$

This implies that the material with an internal energy function $W(\Xi, I_1, I_2)$ experiences actually a *reversible* process from time t_{i-1} to t_{i+1} (see, e.g., Lubliner, 1972).

Let us further think that the dependence of the internal energy function W on the internal variable Ξ is significant from time t_{i-1} to t_{i+1}. (If the dependence of the internal energy function W on the internal variable Ξ is insignificant, the second law of thermodynamics as implied by (A.13) is automatically satisfied with $\partial W/\partial \Xi = 0$.) Therefore, internal energy differs at levels of Ξ_i $(i = 0, 1, 2, \ldots)$, i.e.,

$$W(\Xi_i) < W(\Xi_{i+1}) \quad (i = 0, 1, 2, \ldots). \tag{A.14}$$

Discrepancy of (A.12), however, arises when $(\Xi_{i+1} - \Xi_i) \to \infty$, which means that the internal energy function W has no dependency on Ξ. In order to resolve this, we introduce a concept of "sensitivity" parameter Ξ_c of the material such that internal energy differs at two material states with a difference larger than Ξ_c, i.e.,

$$W(\Xi_i, I_1, I_2) < W(\Xi_i + \Xi_c, I_1, I_2) \tag{A.15}$$

or

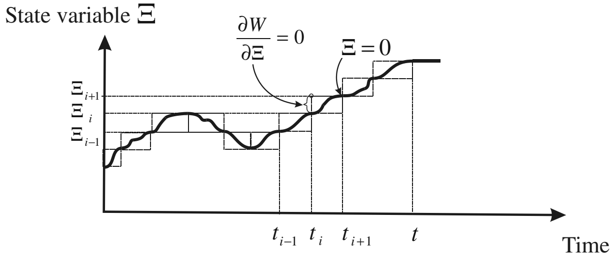

Fig. A.1. A discretized evolution of a state variable.

$$W(\Xi_i + \delta, I_1, I_2) = \begin{cases} W(\Xi_i, I_1, I_2) & 0 \leqslant \delta < \Xi_c, \\ W(\Xi_i + \Xi_c, I_1, I_2) & \delta \geqslant \Xi_c. \end{cases} \tag{A.16}$$

The existence of the "sensitivity" parameter Ξ_c of the material then comprises our second fundamental assumption.

In order for both (A.12) and (A.16) to be true, Ξ_i and Ξ_{i+1} must satisfy a relation that

$$\Xi_{i+1} - \Xi_i \geqslant \Xi_c. \tag{A.17}$$

Let us first assume that $\Xi_{i+1} - \Xi_i > \Xi_c$, therefore we can find a positive value $\tilde{\beta} > 0$ such that $\Xi(= \Xi_i + \Xi_c + \tilde{\beta}) < \Xi_{i+1}$. Since $\Xi \in (\Xi_i, \Xi_{i+1})$, from (A.12), we have

$$W(\Xi, I_1, I_2) = W(\Xi_i, I_1, I_2). \tag{A.18}$$

However, since $\Xi(= \Xi_i + \Xi_c + \tilde{\beta}) > \Xi_i + \Xi_c$, from (A.16), we should have

$$W(\Xi, I_1, I_2) = W(\Xi_i + \Xi_c, I_1, I_2) \tag{A.19}$$

The discrepancy between (A.15) and (A.18) and (A.19) then allows us to say that

$$\Xi_{i+1} - \Xi_i = \Xi_c \tag{A.20}$$

or

$$\Xi_i = \Xi_0 + i\Xi_c. \tag{A.21}$$

At those intervals of Ξ (say $\Xi \in [\beta_1, \beta_2]$) where $\partial W/\partial\Xi \leqslant 0$, similar comments as (A.21) can be addressed. The result (A.21) therefore states that internal energy function W actually shows a *continuous* "step-wise" dependency on the *continuous* internal variable Ξ. While the internal energy function in a form of $W(\Xi, I_1, I_2)$ is *continuous*, it can only alter at certain discrete state variables of $\Xi_0, \Xi_1, \ldots, \Xi_i$ where $\partial W/\partial\Xi \neq 0$ and $\dot{\Xi} = 0$. The transformation between other permissible sources Ψ and the internal energy occurs only at these discrete state variables. The levels of internal energy are, however, undetermined at discrete state variables of $\Xi_0, \Xi_1, \ldots, \Xi_i$. The difference of each discrete state is then characterized by a *sensitivity parameter* Ξ_c (see Fig. A.2).

This is similar to the concepts of "*natural units*" or "*quanta*" discovered by Planck (1901) in study of blackbody radiation, discrete energy levels around a hydrogen atom interpreted by Bohr (1913), and discrete molecular states introduced by Einstein (1917). The authors clearly have no desire to explain the existence of discrete material states

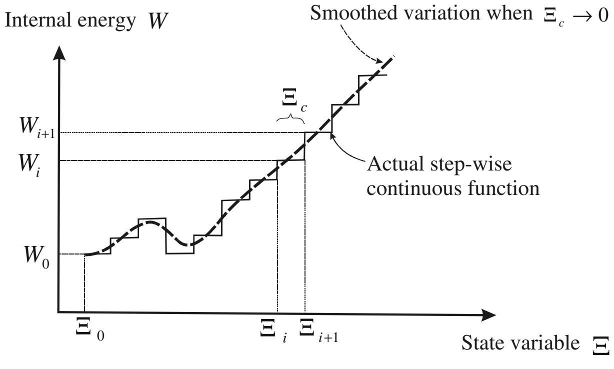

Fig. A.2. A step-wise internal energy function.

$\Xi_0, \Xi_1, \ldots, \Xi_i$ by appeal to these fundamental concepts in physics. They are provided to illustrate the possibility of a continuous step-wise evolution of an internal energy potential (with a basic physical constraint that $|W(\Xi_i, I_1, I_2) - W(\Xi_{i+1}, I_1, I_2)| \geqslant h$, where $h = 6.626 \times 10^{-34}\ \mathrm{m}^2\ \mathrm{kg/s}$ is the Planck's constant).

From (A.16), we know that the level of the internal energy can stay stable with a maximum disturbance of Ξ_c at discrete variables $\Xi_0, \Xi_1, \ldots, \Xi_i$. With $i = 0$, we also know that the original configuration of the material can resist a maximum disturbance of Ξ_c to Ξ_0, i.e.,

$$W(\Xi, I_1, I_2) = W(\Xi_0, I_1, I_2), \quad \Xi \in (\Xi_0 - \Xi_c, \Xi_0 + \Xi_c). \tag{A.22}$$

When Ξ_c is sufficiently small, so is the difference between each evolution step $|\Xi_{i+1} - \Xi_i|$. The continuous step-wise relation between W and Ξ can be approximately smoothed with a continuous form of its slope (shown in Fig. A.2).

Now we interpret the internal variable as the absolute value of the strain rate defined in the paper (i.e., $\Xi = |\dot{\gamma}_0|$). The *original* value of Ξ then becomes $\Xi_0 = 0$. Therefore, there should be an extremely low value of the strain rate $\dot{\gamma}_c$ between which the internal energy function is independent from $\dot{\gamma}_0$, i.e.,

$$W = \begin{cases} W(\dot{\gamma}_c, I_1, I_2), & |\dot{\gamma}_0| \leqslant \dot{\gamma}_c, \\ W(\dot{\gamma}_0, I_1, I_2), & |\dot{\gamma}_0| > \dot{\gamma}_c, \end{cases} \tag{A.23}$$

where W is a *smoothed* function; and $\dot{\gamma}_c$ is called the *rate-independent threshold strain-rate* defined in the paper for model C (see Fig. 7). The detailed experimental procedures for the determination of the form of $W(\dot{\gamma}_0, I_1, I_2)$ and value of $\dot{\gamma}_c$ are described in the paper.

We can further interpret the internal variable as the value of the strain rate (i.e., $\Xi = \dot{\gamma}_0$; see also G'Sell et al., 1985; Marquez-Lucero and G'Sell, 1989; G'Sell and Marquez-Lucero, 1993; Sweeney and Ward, 1995). In this case, the internal variable can take either a positive or a negative form, and $\Xi_0 = 0$. Experimental evidence of strain-rate dependency of an internal energy function is also presented by Pegoretti et al. (2004). In their experiments, the stored energy of a specimen after a loading–unloading cycle was measured using *differential scanning calorimetry* techniques. The stored energy was found to have a positive dependency on both the loading rate and the unloading rate. In most conventional nonlinear viscoelasticity theories, however, materials are assumed to behave nearly elastically at high strain-rates; as such, the stored energy function should be nearly zero at those strain-rates after a loading–unloading cycle. If we assume the internal energy is a function of the strain-rate, such phenomenon can be easily accounted for.

From the preceding analysis, it is then also allowable that the internal energy is independent of $\dot{\gamma}_0$ when $\dot{\gamma}_0 < -\dot{\gamma}_c^{\mathrm{v}}$. As such, the form of the internal energy can have a directional dependency (see also Krempl, 2002; Colak, 2005). The internal energy function can then be written as (see Fig. A.3)

$$W = \begin{cases} \tilde{C}(I_1, I_2), & \dot{\gamma}_0 < -\dot{\gamma}_c^{\mathrm{v}}, \\ W(\dot{\gamma}_c^{\mathrm{v}}, I_1, I_2), & |\dot{\gamma}_0| < \dot{\gamma}_c^{\mathrm{v}}, \\ W(\dot{\gamma}_0, I_1, I_2), & \dot{\gamma}_0 \geqslant \dot{\gamma}_c^{\mathrm{v}}, \end{cases} \tag{A.24}$$

where W is a *smoothed* function for $\dot{\gamma}_0 > \dot{\gamma}_c^{\mathrm{v}}$; $\tilde{C}(I_1, I_2) \geqslant 0$ and $\partial\tilde{C}/\partial\dot{\gamma}_0 = 0$; and $\dot{\gamma}_c^{\mathrm{v}}$ is called the *viscous threshold strain-rate* defined for model A (see also Fig. 7). A physical transition from $\dot{\gamma}_0 < -\dot{\gamma}_c^{\mathrm{v}}$ to $\dot{\gamma}_0 > -\dot{\gamma}_c^{\mathrm{v}}$ must need, however, a finite time that allows the transformation between other forms of energy Ψ with the internal energy to take place.

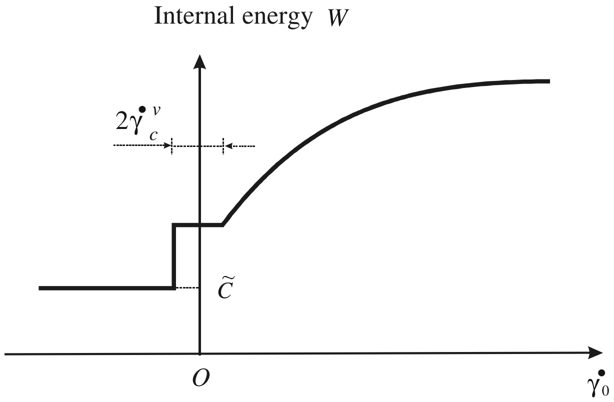

Fig. A.3. Internal energy as a function of strain rate $\dot{\gamma}_0$.

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