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Effects of Cavity Growth and Orientation Hardening on the Stress/Strain Behaviour of Rubber-toughened Plastics

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SUMMARY

Details are presented of extensions to an elastic-plastic model for the non-linear stress/strain behaviour of rubber-toughened plastics. Consideration has been given to the effects of a matrix expansion during plastic deformation on the growth of cavities formed in the rubber particles under dilatational stress fields. The predicted matrix expansion relates to the pressure dependence of the yield stress for the uncavitated material. When this effect is included in the model, good agreement is obtained between the calculated and observed tensile stress/strain behaviour of an acrylonitrile-butadiene-styrene (ABS) plastic. The gradual increase in stress with strain in the post-yield region up to failure has also been considered. This strain hardening is ascribed to molecular orientation which produces an entropy elastic stress contribution that increases with plastic strain. Using relations from the kinetic theory of rubber elasticity, the orientation hardening is characterised by a modulus G_R . For ABS the calculated values of G_R (≈ 5.5 MPa) from tensile and shear data are somewhat lower than values obtained for untoughened glassy plastics, but consistent with the extension of highly entangled polymer chains in the poly(styrene-acrylonitrile) matrix. Further work is proposed to (a) explore the validity of the predicted expansion during plastic deformation for stress states that do not produce cavitation (b) investigate a possible stress-induced structural deageing during yield and (c) incorporate the effects of orientation hardening into the model for the general case of multiaxial loading.

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1 INTRODUCTION

In a previous report¹, an elastic-plastic model was proposed for the stress/strain behaviour of rubber-toughened plastics under multiaxial stress states. The elastic response at low strains was assumed to be linear and isotropic and described by the generalized Hooke's law. The onset of non-linearity in a stress/strain curve was then ascribed to plastic deformation which, for dilatational stress states, is enhanced by the generation and growth of cavities within the rubber particles. Cavities thus form under tension, owing to the dilatational stress component, but not under compression or shear. From shear data, an effective stress may be determined as a function of effective plastic strain for unvoided material. This strain-hardening function is then used, together with a proposed void nucleation criterion, to interrelate the behaviour under different stress states.

For an acrylonitrile-butadiene-styrene (ABS) copolymer containing 38 volume percent rubber, predicted stress/strain curves under uniaxial compression and tension, respectively, were in close agreement with measured curves at 23 °C and an effective strain rate of 0.004 s⁻¹. The model also captured the marked decrease in Poisson's ratio and associated increase in volumetric strain resulting from cavitation during the tensile deformation. However, since these comparisons were limited to strains $\epsilon \leq 0.2$, the effects of cavity growth on the tensile stresses were ignored, as were the effects of orientation hardening which (at low strain rates) became evident at higher levels of strain.

The purpose of this report is to discuss the results of calculations relating both to the growth of cavities and to the influence of molecular orientation on the post-yield region of the stress/strain curves. A summary of the model with proposed extensions to account for cavity growth will be presented in Section 2 of the report. The effects of cavity growth and orientation hardening for the ABS material will then be considered in Sections 3 and 4 respectively.

2 SUMMARY OF THE CONSTITUTIVE RELATIONS

This Section summarises the equations underlying the proposed model and includes (Section 2.5.2) the derivation of a new relationship used to account for the effects of cavity growth.

2.1 ADDITIVITY OF ELASTIC AND PLASTIC STRAINS

In the non-linear region of a stress/strain curve each component of the (true) strain tensor ε_{ij} (1, 2 or 3) is considered as the sum of a recoverable elastic component ε_{ij}^e and a plastic component ε_{ij}^p which is non-recoverable. Thus

$$\varepsilon_{ij} = \varepsilon_{ij}^e + \varepsilon_{ij}^p \quad (1)$$

ELASTICITY EQUATIONS

Assuming linear-elastic behaviour, then components σ_{ij} of the (true) stress tensor are related to the elastic strain components ε_{kl}^e ($k, l = 1, 2, 3$) by

$$\sigma_{ij} = D_{ijkl} \varepsilon_{kl}^e \quad (2)$$

where D_{ijkl} is a component of the fourth-order elasticity tensor and repeated indices indicate summation. For isotropic elasticity

$$D_{ijkl} = \frac{E}{(1 + \nu_e)} \delta_{ik} \delta_{jl} + \frac{E \nu_e}{(1 + \nu_e)(1 - 2\nu_e)} \delta_{ij} \delta_{kl} \quad (3)$$

where E and ν_e are the elastic Young's modulus and the elastic Poisson's ratio, respectively, and δ_{mn} ($m, n = i, j, k, l$) is the Kronecker delta.

2.3 THE YIELD CRITERION

The stress condition for yielding is represented by

$$\Phi = \frac{\sigma_e^2}{\sigma_M^2} - (q_1 f)^2 + 2q_1 f \cosh \left(\frac{3\sigma_k}{2\sigma_M} \right) \left(1 - \frac{\mu\sigma_k}{\sigma_M} \right)^2 = 0$$

where the yield function Φ is defined such that whenever $\Phi < 0$ the response is purely elastic. In this equation, which is based on Gurson's analysis² of plasticity in porous materials, the effective (Mises) stress σ_e is given by

$$\sigma_e = \left(\frac{3}{2} S_{ij} S_{ij} \right)^{1/2}$$

where S_{ij} is a component of the deviatoric stress tensor

$$S_{ij} = \sigma_{ij} - \sigma_k \delta_{ij}$$

and σ_k is the mean normal stress

$$\sigma_k = \frac{\sigma_{ij} \delta_{ij}}{3} = \frac{\sigma_{11} + \sigma_{22} + \sigma_{33}}{3} \quad (7)$$

In equation (4), f is the effective volume fraction of cavities which increases with strain as discussed in Section 2.5. The parameter q_1 , was introduced by Tvergaard³ and accounts for the effect of void interactions on the stress distribution in the matrix between cavities. The parameter μ was introduced by Lazzeri and Bucknall⁴ to allow for the dependence of yield stress on σ_k in the absence of voids ($f=0$). The yield stress σ_M is $\sqrt{3} \times$ the shear yield stress for the matrix material between voids and is discussed further in Section 2.6.

2.4 THE FLOW RULE

For associated flow, increments of plastic strain are given by the flow rule

$$d\epsilon_{ij}^p = d\lambda \frac{\partial \Phi}{\partial \sigma_{ij}} \quad (8)$$

where $d\lambda$ is a scalar multiplier. Ignoring the effects on Φ of varying σ_M and f we obtain from (4)

$$d\epsilon_{ij}^p = d\lambda \left\{ \frac{3S_{ij}}{\sigma_M^2} + \left[\frac{q_1 f}{\sigma_M} \sinh \left(\frac{3\sigma_k}{2\sigma_M} \right) + \frac{2\mu}{3\sigma_M} \left(1 - \frac{\mu\sigma_k}{\sigma_M} \right) \right] \delta_{ij} \right\} \quad (9)$$

With the aid of the plastic work equivalence

$$\sigma_{ij} d\epsilon_{ij}^p = (1-f) \sigma_M d\epsilon_0^p$$

it follows that

$$\begin{aligned} d\lambda &= \frac{(1-f) \sigma_M d\epsilon_0^p}{\sigma_{ij} \partial \Phi / \partial \sigma_{ij}} \\ &= \frac{(1-f) \sigma_M d\epsilon_0^p}{\sigma_{ij} \left\{ \frac{3S_{ij}}{\sigma_M^2} + \left[\frac{q_1 f}{\sigma_M} \sinh \left(\frac{3\sigma_k}{2\sigma_M} \right) + \frac{2\mu}{3\sigma_M} \left(1 - \frac{\mu\sigma_k}{\sigma_M} \right) \right] \delta_{ij} \right\}} \end{aligned}$$

In these equations the effective matrix plastic strain ϵ_0^p is assumed to be independent of rubber content in the matrix, and hence of the void fraction (Section 2.6). From equations (10), (4) and (21) below with $f=0$ it follows that $\epsilon_0^p = \gamma^p / \sqrt{3}$ where γ^p is the plastic strain determined in a shear test on the unvoided, rubber-toughened material.

VOID NUCLEATION AND GROWTH

During an increment of applied strain, the change in void volume fraction df is considered as the sum of a contribution df_{nucl} from nucleation and a contribution df_{gr} from void growth, so

$$df = df_{\text{nucl}} + df_{\text{gr}} \quad (12)$$

Nucleation

It is assumed that cavities are generated only in the rubber particles and that each particle offers negligible resistance to deformation once a small cavity has formed. The nucleation process is then regarded as involving the progressive replacement of rubber particles by an equal volume of effective voids. From the work of Bucknall and coworkers^{4,5}, we assume that the nucleation of a cavity in a given rubber particle occurs at some critical volumetric strain in the particle that increases with the rubber shear modulus and surface energy and decreases with increasing particle diameter. For a distribution of particle sizes, the nucleation should then occur over a range of total volumetric strain (ϵ_v) related to the critical volumetric strain range for the rubber particles

It was proposed¹ that f_{nucl} is zero for volumetric strains up to some initial value ϵ_{1v} and subsequently increases with ϵ_v according to a stretched-exponential function

$$f_{\text{nucl}} = 0 \quad \text{for } \epsilon_v \leq \epsilon_{1v} \quad (13a)$$

$$f_{\text{nucl}} = v_{R0} \left\{ -\exp \left[\left(\frac{\epsilon_v - \epsilon_{1v}}{\epsilon_{2v}} \right)^{\beta_v} \right] \right\} \quad \text{for } \epsilon_v > \epsilon_{1v} \quad (13b)$$

In equation (13b) the parameters ϵ_{2v} and β_v ($0 < \beta_v \leq 1$) determine the location and breadth of the volumetric strain range over which void nucleation occurs.

2.5.2 Growth

The growth of voids following their nucleation occurs through plastic deformation within the matrix material. In deriving a relation for df_{gr} , we denote by V , V_v and V_M the instantaneous values of total volume, void volume and matrix volume, respectively, during growth. [Note that some voids will commence growth before others have been nucleated. V_M is then equated to $V_R + V_{pl}$ where V_R and V_{pl} are the respective volumes of unvoided rubber and plastic material in the matrix]. The void fraction f is given by

$$f = \frac{V_v}{V} = \frac{V_v}{V_M + V_v} \quad (14)$$

and df_{gr} is calculated using

$$df_{gr} = \left(\frac{\partial f}{\partial V_v} \right) dV_v^p + \left(\frac{\partial f}{\partial V_M} \right) dV_M^p$$

where dV_v^p and dV_M^p are the incremental changes in void volume and matrix volume, respectively, due to plastic deformation in the matrix. From (14) and (15) we obtain

$$\begin{aligned} df_{gr} &= (1-f) \frac{dV_v^p}{V} - f \frac{dV_M^p}{V} \\ &= (1-f) \frac{dV^p}{V} - \frac{dV_M^p}{V} \end{aligned}$$

where $dV^p (= dV_v^p + dV_M^p)$ is the total incremental plastic volume change. Writing equation (16) in the form

$$df_{gr} = (1-f) d\epsilon_{ij}^p \delta_{ij} - (d\epsilon_{ij}^p \delta_{ij})_{f=0}$$

we obtain, using (9),

$$df_{gr} = \frac{d\lambda}{\sigma_M} \left[3q_1 f (1-f) \sinh\left(\frac{3\sigma_k}{2\sigma_M}\right) \left(\frac{\mu\sigma_k}{\sigma_M} \right) \right]$$

2.6 EVOLUTION OF THE MATRIX COMPOSITION AND YIELD STRESS σ_M

Since void nucleation is assumed to involve the replacement of rubber particles with an equal effective volume of cavities, the instantaneous volume fraction v_R^* of unvoided rubber in the “matrix” surrounding the voids will decrease as the nucleation proceeds. If v_{R0} is the initial volume fraction of rubber particles it follows that¹

$$v_R^* = \frac{v_{R0} - f_{nucl}}{1 - f_{nucl}}$$

The decrease in v_R^* can give rise to a marked increase in the matrix yield σ_M during the nucleation. Assuming that σ_M increases linearly with v_R^* we have obtained

$$\sigma_M = \sigma_{01} (1 - kv_R^*)$$

$$\frac{\sigma_0(\varepsilon_0^p)}{1 - kv_{R0}} \left[1 - k \left(\frac{v_{R0} - f_{nucl}}{1 - f_{nucl}} \right) \right]$$

Here σ_0 and σ_{01} are the values of $\sqrt{3}\sigma_S$ for the unvoided material with and without rubber particles, respectively, where σ_S is the shear yield stress. The constant k specifies the dependence of shear yield stress on the volume fraction of rubber particles for unvoided material. The variation of σ_0 with ε_0^p can be determined from shear tests on the unvoided material and represents the basic hardening data required in applications of the model.

2.7 MODELLING THE STRAIN HARDENING FUNCTION

The dependence of σ_0 on ε_0^p can be supplied as input data either in numerical form or in terms of the parameters of some function fitted to the data. Figure 1 illustrates the variation of σ_0 with ε_0^p for the ABS material with $\nu_{R0} = 0.38$. Following an initial rapid rise, the value of σ_0 reaches a plateau at an effective plastic strain ε_0^p of about 0.03. Over this ε_0^p range the data can be fitted with the stretched exponential function

$$\sigma_0 = \sigma_{0I} + (\sigma_{0F} - \sigma_{0I}) \left\{ 1 - \exp \left[-(\varepsilon_0^p / \varepsilon_{0S})^{\beta_0} \right] \right\} \quad (22)$$

where σ_{0I} is the initial yield stress associated with the onset of nonlinearity and σ_{0F} is the flow stress corresponding to the plateau in the curve at $\varepsilon_0^p = 0.03$. The parameters ε_{0S} and β_0 characterise the rate at which σ_0 increases with ε_0^p . The values for each of these parameters, giving the fit illustrated in Figure 1, are included in Table

In the post-yield region ($\varepsilon_0^p > 0.03$), σ_0 initially exhibits a slight decrease and a subsequent increase from ε_0^p values above about 0.1. Although the data in this region are subject to experimental uncertainties, these effects are thought to reflect possible structural changes and subsequent orientational hardening resulting from the yield process. The incorporation of such effects into the model will be commented on in Section 4 below.

2.8 SUMMARY OF THE MODEL PARAMETERS OBTAINED FOR ABS

Table 1 lists the values of the parameters determined for the ABS material containing 38% rubber by volume. The methods employed in these evaluations were described in detail previously¹. They involved analyses of stress/strain data at 23 °C using a combination of uniaxial tension, shear and uniaxial compression tests. The strain rates used in the tensile and compressive tests were close to the effective strain rate ($\dot{\varepsilon}_0^p = \dot{\gamma}^p / \sqrt{3}$) in the shear test of 0.004 s⁻¹.

Table 1 – Values of Parameters for ABS
at 23 °C and 0.004 s⁻¹

E (MPa)	2,300	ϵ_{1V}	0.004	σ_{0I} (MPa)	15
ν_e	0.39	ϵ_{2V}	0.0021	σ_{0F} (MPa)	48
ν_{R0}	0.38	β_v	0.65	ϵ_{0S}	0.003
k	1.35			β_0	0.7
μ	0.22				
q_1	1.57				

3 EFFECTS OF CAVITY GROWTH ON THE TENSILE STRESS/STRAIN BEHAVIOUR

Using the values of parameters given in Table 1, a numerical method was employed for solving the elasticity, yield and flow equations in Section 2 in order to calculate the variations of tensile stress, volumetric strain and effective void fraction with applied uniaxial strain. In these calculations contributions to f from void growth, allowing for possible matrix expansion, were included through the use of equations (12), (13) and (18).

Figures 2, 3 and 4 compare the results of the above calculations with the results of similar calculations which allow for cavity growth but assume that the matrix volume is unchanged (whilst retaining the parameter μ in the flow equation (9)). In this case the second term on the right hand side of equations (16) and (17) is ignored and in place of (18) we obtain

$$df_{gr} = (1-f) \frac{d\lambda}{\sigma_M} \left| \left(\frac{3\sigma_k}{2\sigma_M} \right) + 2\mu \left(\frac{\mu\sigma_k}{\sigma_M} \right) \right| \quad (23)$$

The measured tensile stresses σ_T are also shown as a function of strain ϵ_T in Figure 3, and Figure 4 includes the experimental values of volumetric strain ϵ_V obtained from the measured Poisson's ratio ν ($\epsilon_V = \epsilon_T(1-2\nu)$).

From Figure 2 we note that the calculated f values are largest when the growth occurs without matrix expansion. This gives rise to relatively low calculated values of σ_T (Fig 3) and high ϵ_v values (Fig 4). Although the discrepancies between the observed and calculated stresses could be offset by the effects of molecular orientation, it is unlikely that the magnitude of orientation hardening would be sufficiently large at such low strains. When allowance is made for possible matrix expansion during void growth, the calculated and measured stresses are in close agreement (Fig 3) and the predicted ϵ_v values are also closer to the experimental values (Fig 4).

It is also of interest to note that the calculated values of f , σ_T and ϵ_v , allowing for the possible effects of matrix expansion, are hardly distinguishable from the respective values previously predicted assuming $f = f_{\text{nucl}}$ and thus ignoring cavity growth. This suggests that, for the values of μ and f applicable to the ABS material, the predicted expansions of voids and matrix are such as to produce a negligible change in volume fraction of voids and hence a negligible contribution to f from void growth.

Some comment should be made on the above results relating to the apparent influence of matrix expansion in limiting the magnitude of the calculated cavity growth. For uncavitated polymers it is widely considered that any volume increases during yield are very small despite the established increase in yield stress with applied pressure (or negative hydrostatic stress). The latter is generally ascribed to a decrease in molecular mobility associated with a positive activation volume. With the elastic-plastic models, however, the dependence of yield stress on hydrostatic stress is intrinsically associated with volume increases since, for associated flow, the parameter μ in the yield function (4) appears in the flow rule (9) for the normal components of plastic strain. In fact, for different stress states with $f=0$ (including pure shear and uniaxial compression) the flow rule predicts that the plastic component of volumetric strain ϵ_v^p is equal to $\mu\epsilon_0^p$, corresponding to a material expansion.

If it is accepted that volume changes are negligible during the yield of uncavitated plastics, it may be possible to retain the parameter μ in the yield function but to put $\mu=0$ in the flow rule. This would represent an extreme case of non-associated flow (or deviation from the normality condition) and for cavitating materials equation (23) would be replaced by

$$df_{gr} = \frac{d\lambda}{\sigma_M} \left(\begin{array}{c} \\ \end{array} \right)$$

Using equation (24), the predicted values of f , σ_T and ε_v should lie between the values calculated on the basis of (18) and (23). The derived values of σ_T will again be lower than the experimental values but the discrepancy might now be offset by orientation hardening.

Calculations based on equation (24) have not yet been undertaken and could be considered in future work. However it would seem more important to establish whether any significant volume increases occur during yield for stress states, such as shear or uniaxial compression, that do not produce cavitation. From the results of such experiments an assessment could be made of the general validity of the elastic-plastic model and, in particular, the use of the yield function Φ as given by (4) to represent the “plastic potential” as in equation (8).

4 ORIENTATION HARDENING

4. TENSION

The effects of molecular orientation in the post-yield region are most evident in the tensile data. Figure 5 illustrates the tensile stress/plastic strain curves determined at 23 °C and different strain rates using methods described previously⁶. At low strain rates, the strain softening and subsequent plateau at plastic strains between about 0.004 and 0.15 is associated with cavitation and has been modelled as described in Section 2. A gradual increase in stress, ascribed to orientation hardening, is then observed at higher strains up to failure. With increasing strain rate the softening due to cavitation is reduced and the orientation hardening is evident at progressively lower strains.

Contributions to the stress from molecular orientation are usually considered to arise from the decrease in entropy as the polymer chains extend to less probable configurations. From the kinetic theory of rubber elasticity⁷, assuming Gaussian chain statistics, we obtain the following relation for the difference between the principal entropy elastic stresses σ_{1R} and σ_{2R}

$$\sigma_{1R} - \sigma_{2R} = G_R (\lambda_1^2 - \lambda_2^2)$$

Here G_R is a “rubberlike” shear modulus given by $G_R = NkT$ where N is the number of chains per unit volume between entanglement points in the network, k is Boltzmann’s constant and T the absolute temperature. Symbols λ_1 and λ_2 are principal plastic extension ratios (omitting the p superscript), where λ_i ($i = 1, 2, 3$) is related to the true plastic strain ϵ_i^p by $\lambda_i = \exp(\epsilon_i^p)$. Owing to the use of Gaussian chain statistics, equation (25) is valid up to moderate λ_i values such that the chain extensions do not exceed about one half their maximum extension. An alternative equation, based on Langevin chain statistics has been employed to model orientation hardening up to very large strains⁸

Under uniaxial tension we put $\sigma_{1R} = \sigma_{TR}$, $\sigma_{2R} = 0$, $\lambda_1 = \lambda$ and, ignoring small volume changes, $\lambda_2^2 = \lambda_1^{-1} = \lambda^{-1}$. Equation (25) then becomes

$$\sigma_{TR} = G_R (\lambda^2 - 1/\lambda)$$

where $\lambda = \exp(\epsilon_T^p)$. In applying this equation to the analysis of the tensile data, we estimated the “rubberlike” stress σ_{TR} by subtracting from the total stress σ_T the measured total stress at a selected plastic strain $\epsilon_{T,min}^p$ such that plots of σ_{TR} versus $(\lambda_a^2 - 1/\lambda_a)$ are approximately linear. The apparent plastic extension ratio λ_a is given by

$$\lambda_a = \exp(\epsilon_T^p - \epsilon_{T,min}^p)$$

and, in accordance with (26),

$$\sigma_{TR} = G_R (\lambda_a^2 - 1/\lambda_a)$$

The value of $\epsilon_{T,min}^p$ is considered to represent that plastic strain above which contributions to the varying σ_T become constant.

Figure 6 shows the estimated stresses σ_{TR} plotted against $(\lambda_a^2 - 1/\lambda_a)$ for the ABS at different strain rates together with the selected values of $\varepsilon_{T,min}^p$. Within the rather large experimental scatter, the results are consistent with an orientation hardening characterised by a modulus $G_R = 5.5$ MPa. This is somewhat lower than values (8-18 MPa) reported for untoughened glassy plastics in the post-yield region⁸, due probably to the large fraction of rubber or voids dispersed in the poly(styrene acrylonitrile) plastic. However the derived G_R value is about 50 times higher than the shear moduli of crosslinked rubbers, reflecting the high entanglement density in the polar glassy polymer matrix. In this context, a similar analysis of our tensile data for ABS at 0 °C gave $G_R = 6.5$ MPa. This result indicates that the effective entanglement density increases with decreasing temperature, as reported for other glassy polymers⁸. From Figure 6 we also note that the selected values of $\varepsilon_{T,min}^p$ tend to decrease with increasing strain

This reflects the apparent shift of the onset of orientation hardening to lower strains and is attributed to the reduced effect of softening produced by the cavitation.

SHEAR

As noted in Section 2.7, the gradual increase in σ_0 with ε_0^p for ε_0^p values above about 0.1 (Fig 1) is thought to reflect a contribution to the shear stress from molecular orientation. For the case of pure shear we put $\sigma_{2R} = -\sigma_{1R}$, $\sigma_{SR} = (\sigma_{1R} - \sigma_{2R})/2 = \sigma_{1R}$, $\sigma_{3R} = 0$ and ignoring any small volume change, $\lambda_2 = 1/\lambda_1 = 1/\lambda$ and $\lambda_3 = 1$. From equation (25) the entropic stress/strain relation then becomes

$$\sigma_{SR} = \frac{G_R}{2} (\lambda^2 - 1/\lambda^2) \quad (29)$$

The extension ratio λ is now related to the plastic shear strain γ^p by $\lambda^2 = \exp(\gamma^p)$ which follows from $\gamma^p = \varepsilon_1^p - \varepsilon_2^p = 2\varepsilon_1^p = 2\ln\lambda_1 = 2\ln\lambda$. Making the substitutions $\sigma_{OR} = \sqrt{3}\sigma_S$ and $\varepsilon_0^p = \gamma^p/\sqrt{3}$, we then obtain for the entropic contribution σ_{OR} to the effective stress σ_0

$$\sigma_{OR} = \frac{\sqrt{3}}{2} G_R (\lambda^2 - 1/\lambda^2) \quad (30)$$

where $\lambda^2 = \exp(\sqrt{3} \varepsilon_0^p)$

Figure 7 shows values of σ_{OR} derived from the data of Figure 1 by subtracting from the σ_0 values at higher strains the measured σ_0 at $\varepsilon_{0,min}^p = 0.11$. An approximately linear variation of σ_{OR} with $(\lambda_a^2 - 1/\lambda_a^2)$ is then obtained where $\lambda_a^2 = \exp[\sqrt{3}(\varepsilon_0^p - \varepsilon_{0,min}^p)]$. In accordance with equation (30), the slope of the plot in Figure 7 gives $G_R = 5.7$ MPa. This value is close to that obtained from the tensile data.

The small decrease in σ_0 as ε_0^p increases from 0.03 to 0. (Fig 1) suggests that the σ_{OR} contribution is initially offset by a contribution from strain softening. A similar softening effect was observed under uniaxial compression¹ and, in the shear tests, the magnitude of the effect increased somewhat with increasing strain rate. These results indicate that the softening involves a structural deageing of the (uncavitated) material. Similar effects have been observed by Boyce⁸ for PMMA and other glassy plastics and correlated with a dilatation and associated increase in internal energy during shear yielding. The softening could be modelled by taking the flow stress σ_{OF} and initial yield stress σ_{OI} in equation (22) to decrease slightly with ε_0^p toward constant values at a plastic strain ($\varepsilon_{0,min}^p$) for which the structure has obtained a steady state. The decreases in σ_{OF} and σ_{OI} could, in turn, be related to increases in activation volume V or decreases in a related parameter $A = R/V$. This parameter has been introduced elsewhere⁶ as part of the Eyring flow model for describing the rate and temperature dependence of σ_0 .

4.3 MULTIAXIAL LOADING

Different approaches may be considered for incorporating the contributions from orientation hardening into the multiaxial stress/strain relationships in Section 2. The first of these is to add the entropic stress σ_{OR} given by equation (30) to the (microscopic) effective matrix stress

σ_0 in equation (22). Since the orientation is generated in the matrix material, this represents the simplest and most basic method of implementation. However there is some uncertainty as to whether this method would capture the highly anisotropic nature of the orientation effect.

Another approach is based on the model introduced by Haward and generalized by Boyce⁸. This model comprises a linear energy-elastic spring in series with a non-linear entropy-elastic spring and a dashpot, the two latter elements acting in parallel. The total (macroscopic) strain ϵ_{ij} is again the sum of contributions ϵ_{ij}^e and ϵ_{ij}^p where ϵ_{ij}^e is the strain on the linear spring and ϵ_{ij}^p is the plastic strain on both the non-linear spring and the dashpot. The total (macroscopic) stress σ_{ij} is given by

$$\sigma_{ij} = \sigma_{ij}^e = \sigma_{ijR} + \sigma_{ijV} \quad (31)$$

where σ_{ij}^e , σ_{ijR} and σ_{ijV} are stresses on the linear spring, the non-linear (rubberlike) spring and the (viscous) dashpot respectively. The elasticity equations of Section 2.2 will still apply with $\sigma_{ij} = \sigma_{ij}^e$. However the stress σ_{ij} in the yield and flow equations (Sections 2.3 and 2.4) must be replaced by $\sigma_{ijV} = \sigma_{ij} - \sigma_{ijR}$. This illustrates that the chain orientation produces an internal backstress which serves to reduce the fraction of the applied stress which acts on the dashpot. The stress components σ_{ijR} may be derived from the principal network stresses σ_{iR} using relations underlying (25) and a value of G_R determined as above from tensile data. The incorporation of orientation hardening data into the model could possibly involve a combination of the approaches outlined above, and there is a need to ascertain the validity of the yield criterion (4) for high levels of structural anisotropy

5 CONCLUSIONS

The calculated and observed tensile behaviour of ABS are in good agreement when allowance is made for the effect of matrix expansion during yield in limiting the growth of cavities generated in the rubber particles.

- The predicted matrix expansion is related to the dependence of yield stress on the hydrostatic stress component for non-cavitated materials. This is represented in the yield function (4) by the factor μ which then appears in the flow equations (9) for the normal increments of plastic strain.
- There is a need to establish whether, in fact, any volume increases occur during yield for stress states, such as pure shear or uniaxial compression, that do not induce cavitation.
- A gradual increase in yield stress with strain in the post-yield region for ABS is ascribed to the effect of orientation hardening. Using relations from the kinetic theory of rubber elasticity, this can be described by an entropic stress contribution from polymer chain extension in a highly entangled network.
- There is a need to explore whether, in addition to cavitation, a stress-induced structural deageing may offset the effect of orientation at low plastic strains.

Further developments are required to incorporate the stress contributions from molecular orientation into the model for the general case of multiaxial loading.

6 ACKNOWLEDGEMENT

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REFERENCES

- 1 B.E. Read, G.D. Dean and L. Wright. A proposed model for the non-linear stress/strain behaviour of rubber-toughened plastics. NPL report CMMT(A)301 (2000).
- 2 A.L. Gurson. J. Eng. Mater. Technol., Trans. ASME 99 (1977) p2.
- 3 V. Tvergaard. Int. J. Fract. Mech., 17 (1981) p389.
- 4 A. Lazzeri and C.B. Bucknall. J. Mat. Sci., 28 (1993) p6799.
- 5 C.B. Bucknall. in The Physics of Glassy Polymers, Second edition (edited by R.N. Haward and R.J. Young), Chapman and Hall, London (1997), Chapter 8, p363.
- 6 B.E. Read, G.D. Dean and B.C. Duncan. Characterisation of the strain rate and temperature dependence of the properties of plastics for the prediction of impact performance. NPL Report CMMT(A)144 (1999).
- 7 L.R.G. Treloar. The Physics of Rubber Elasticity, Third edition, Clarendon Press, Oxford, UK (1975).
- 8 M.C. Boyce and R.N. Haward. in The Physics of Glassy Polymers, Second edition (edited by R.N. Haward and R.J. Young), Chapman and Hall, London (1997), Chapter 5, p213.

FIGURE CAPTIONS

Fig Variation of effective stress σ_0 with effective plastic strain ε_0^p from shear data for ABS (◆) at 23 °C and $\dot{\varepsilon}_0^p = 0.004 \text{ s}^{-1}$. The continuous line was calculated using equation (22) with values of the parameters given in Table 1

Calculated dependence of the effective void fraction f on tensile strain including the effect of cavity growth either with (equation (18)) or without (equation (23)) matrix expansion.

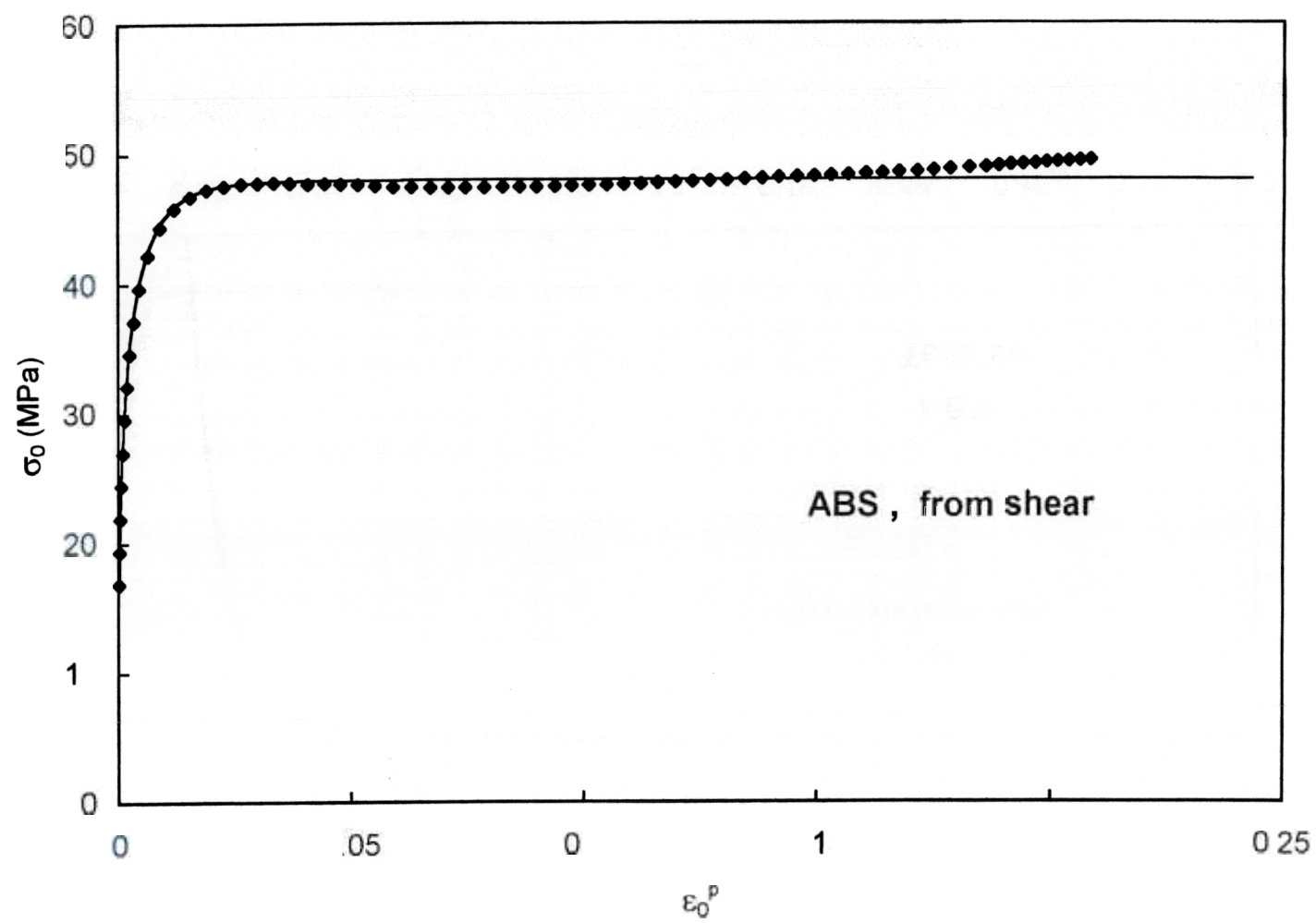
Comparison of the measured (■) stress/strain curve in uniaxial tension with predicted curves allowing for cavity growth either with or without matrix expansion.

Comparison of the measured (■) dependence of volumetric strain on tensile strain with predicted variations allowing for cavity growth either with or without matrix expansion.

Experimental variation of tensile stress versus plastic strain at the strain rates (s^{-1}) indicated on each curve.

Fig 6 Variation of the entropic contribution σ_{TR} to the tensile stress with $\lambda_a^2 - 1/\lambda_a$. Point symbols were calculated from the experimental data at the strain rates indicated. Numbers in brackets are values of $\varepsilon_{T,\min}^p$ used in deriving the plastic extension ratios λ_a according to equation (27). The continuous line was obtained using equation (28) with the indicated value of G_R

Fig 7 The entropic contribution σ_{0R} to the effective stress σ_0 plotted against $\lambda_a^2 - (1/\lambda_a)^2$. Point symbols (■) were calculated from the experimental data at 0.004 s^{-1} using $\varepsilon_{0,\min}^p = 0.11$ to derive the value of λ_a as described in the text. The continuous line was obtained using equation (30) with the indicated value of G_R .



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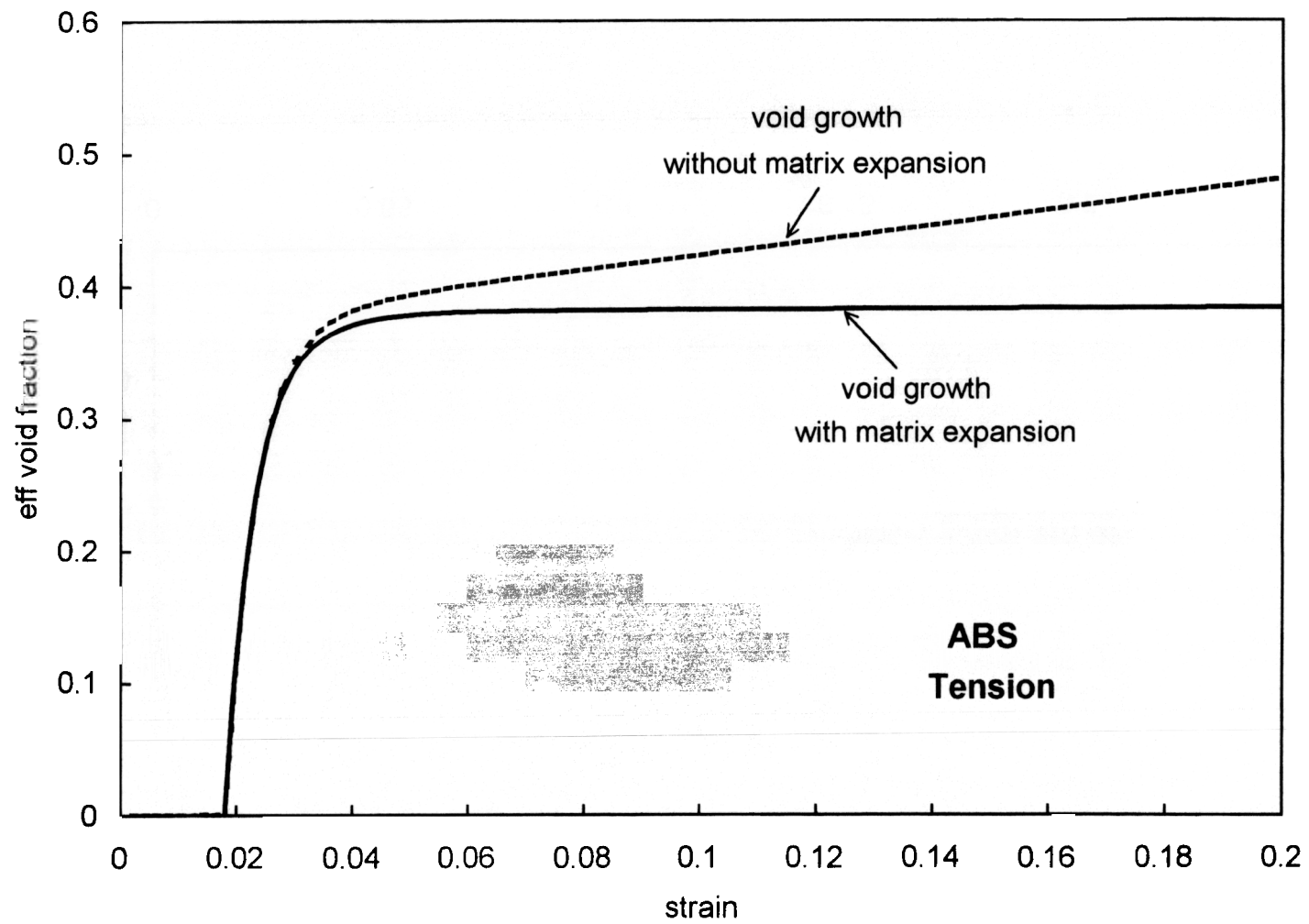


Fig. 2

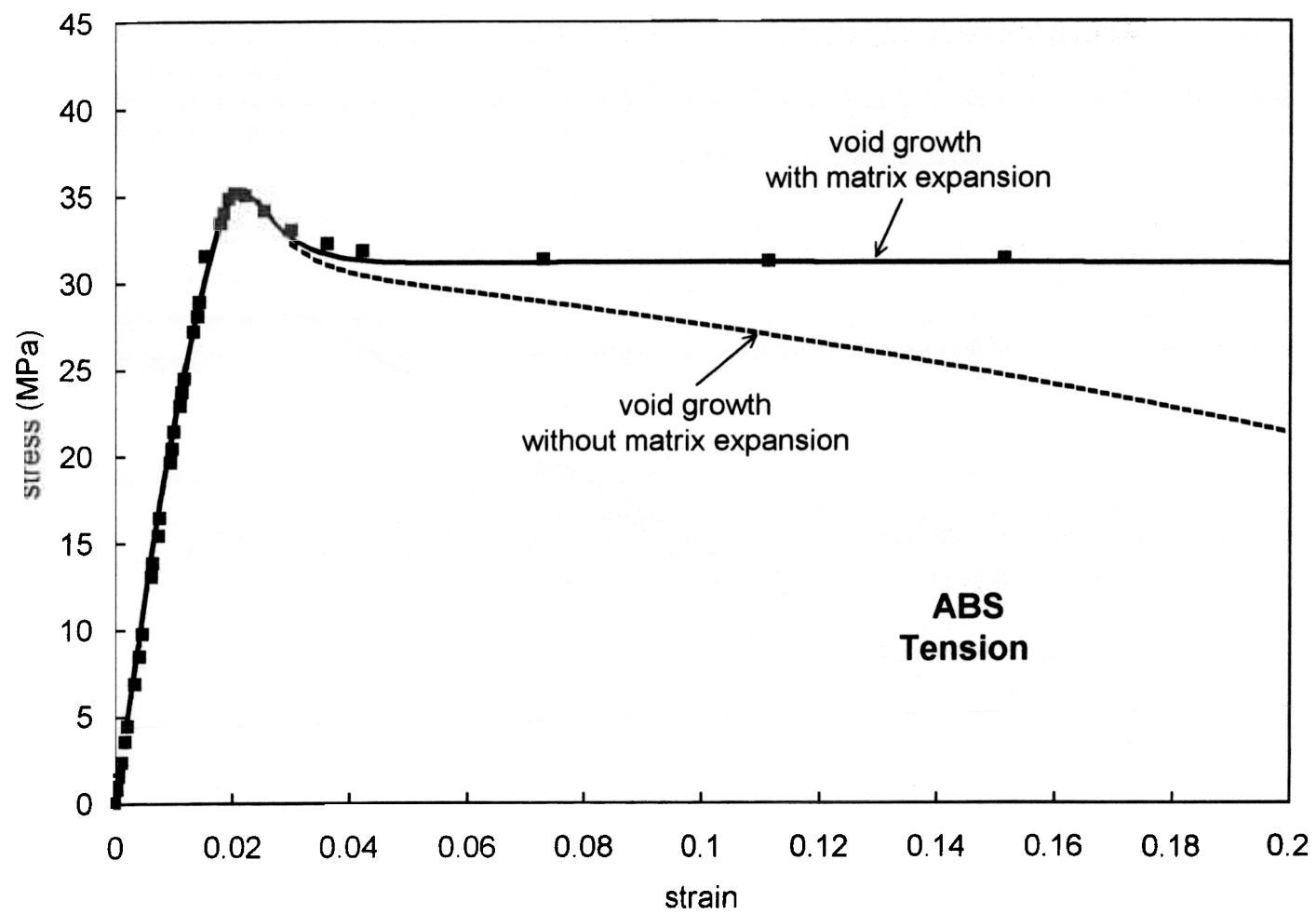


Fig. 3

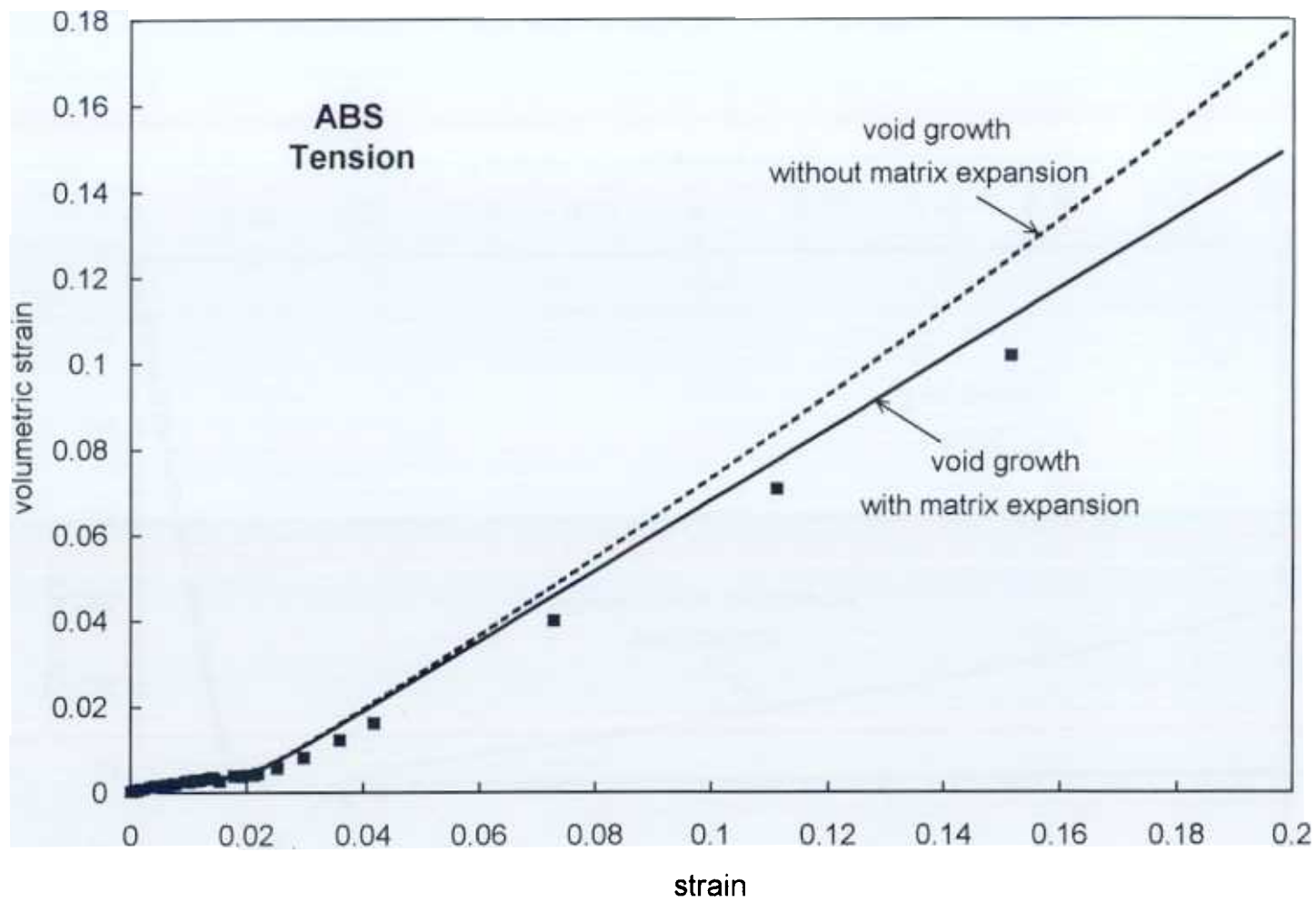


Fig. 4

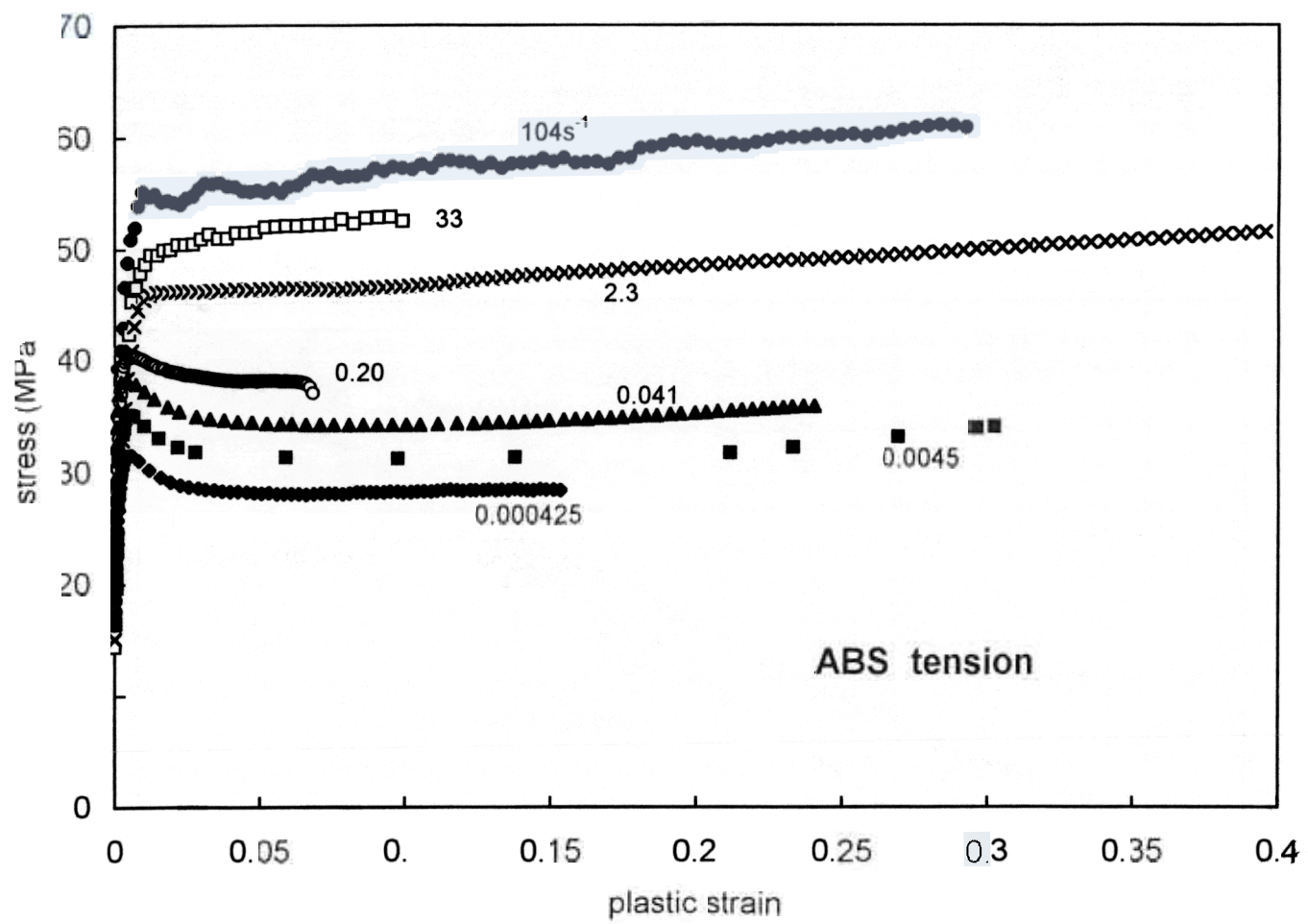
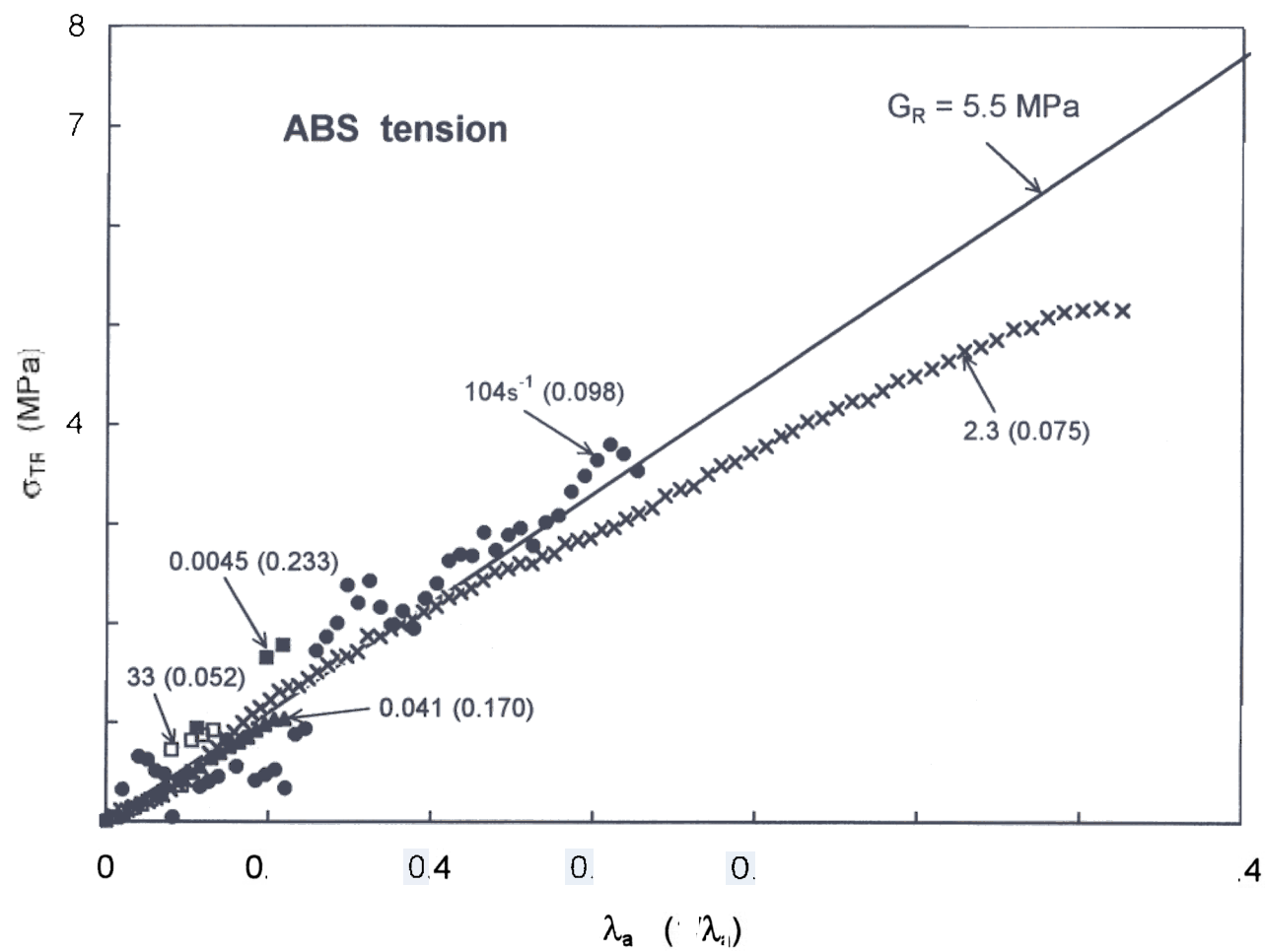


Fig. 5



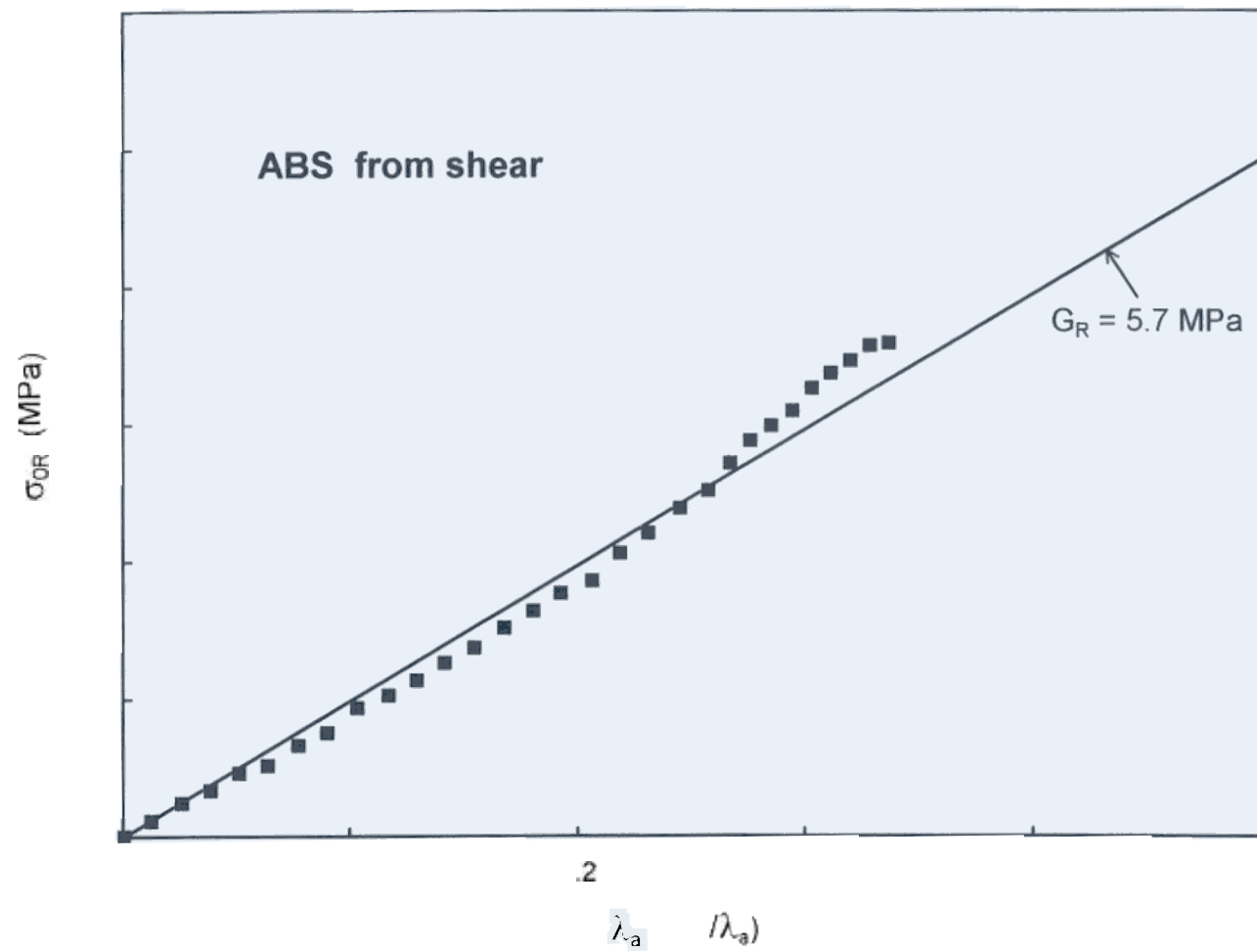


Fig 7