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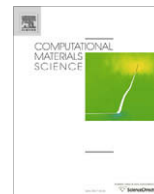
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A cell model study of crazing and matrix plasticity in rubber-toughened glassy polymers

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ABSTRACT

The competition between crazing and matrix shear yielding in rubber-toughened glassy polymers is investigated by detailed finite element simulations. To this end the microstructure is represented by an axisymmetric unit cell of glassy matrix containing a single cavitated rubber particle which is modeled as a void. The behavior of the matrix material is described in the framework of finite strain viscoplasticity while a cohesive surface model is employed for crazing. The influence of the matrix yield behavior, the craze response, the rubber content, and the overall loading state are analyzed.

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1. Introduction

The enhanced ductility and fracture toughness of rubber-toughened glassy polymers results from dissipative micromechanisms initiated at rubber particles that are finely dispersed in the glassy matrix and act as stress concentrators at many sites throughout the material. In ABS (acrylonitrile–butadiene–styrene) two distinctly different inelastic deformation mechanisms – shear yielding and crazing – are observed, and their interaction depends on a variety of factors such as the yield behavior of the glassy matrix, the size and volume fraction of the rubber particles, and the overall loading conditions (e.g. [4]). Though a qualitative picture of these interrelations has emerged from a large number of experimental studies (e.g. [2,9,11]), a deeper understanding and theoretical framework is so far lacking. Micromechanical modeling and numerical simulations, therefore, are hoped to provide some additional insight.

Previous studies, in this regard, have focused either on sole yielding (without crazing) of the matrix around rubber particles (e.g. [17,5,12]) or on crazing in an otherwise elastic medium [16]. The present work takes both mechanisms into account and thus is a first step towards analyzing their interaction and the resulting effects on the material's overall response. Special attention is paid

– by means of appropriate parameter variations – to the influence of the initial matrix yield behavior and the stress-carrying response of the crazes; this effect is hardly accessible to direct measurement and hence quite unclear.

2. Problem formulation

2.1. Unit cell modeling of ABS microstructure

ABS consists of an amorphous thermoplastic SAN (styrene–acrylo–nitrile) matrix which contains sub-micron sized rubber particles of a volume fraction up to 40%. As a simplified model of the microstructure, a periodic arrangement of rubber particles in a stacked hexagonal array is considered here, subjected to loading in terms of macroscopic principal stresses $\Sigma_{1,2,3}$ along the symmetry axes (Fig. 1a). This morphology can be approximated by an axisymmetric unit cell (Fig. 1b). Since the rubber particles typically cavitate in the early stage of loading and thereafter have a negligible stiffness they are treated as voids.

Crazes are localized zones which form perpendicular to the direction of maximum principal stress. The latter coincides with the three-direction in the present model by choosing $\Sigma_3 > \Sigma_1 = \Sigma_2$; hence crazing is expected to take place in the ring-shaped equator plane of the rubber particles (voids). It is described by means of a cohesive surface model (see Fig. 1b and c), details of which are discussed in Section 2.3.

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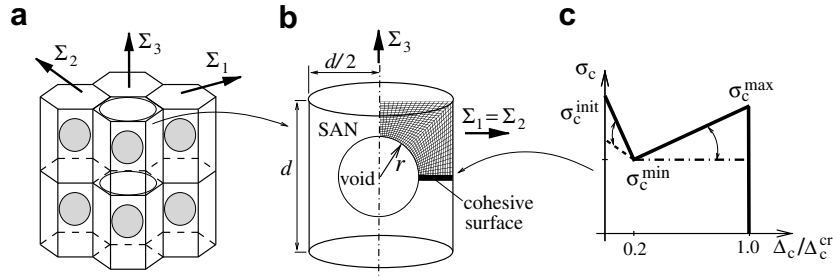


Fig. 1. (a) Model microstructure with stacked hexagonal array of rubber particles in SAN matrix, (b) axisymmetric unit cell model employed in numerical analysis, and (c) different variations of cohesive strength as a function of separation considered in the crazing model.

2.2. Deformation behavior of glassy matrix

A now well-established constitutive model for the large strain visco-plastic deformation behavior of glassy polymers has originally been developed by Boyce et al. [3] and was later on modified by Wu and Van der Giessen [19]. The latter version, in conjunction with material parameters reported in [17], is employed here for the SAN matrix. It makes use of the additive decomposition of the strain rate tensor into its elastic and plastic parts, $\mathbf{D} = \mathbf{D}^e + \mathbf{D}^p$, where the former is governed by the hypoelastic relation $\mathbf{D}^e = \mathcal{L}^{-1} \dot{\bar{\boldsymbol{\sigma}}}$ with \mathcal{L} the isotropic elasticity tensor and $\dot{\bar{\boldsymbol{\sigma}}}$ the Jaumann rate of the Cauchy stress tensor. Isochoric rate and temperature dependent plastic flow is described by

$$\mathbf{D}^p = \frac{\dot{\gamma}^p}{\sqrt{2}\tau} \bar{\boldsymbol{\sigma}}', \quad \dot{\gamma}^p = \dot{\gamma}_0 \exp \left[-\frac{A\tilde{s}}{\theta} \left(1 - \left(\frac{\tau}{\tilde{s}} \right)^{5/6} \right) \right],$$

$$\tau = \sqrt{\frac{1}{2} \bar{\boldsymbol{\sigma}}' \cdot \bar{\boldsymbol{\sigma}}'} \quad (1)$$

where $\bar{\boldsymbol{\sigma}}' = \bar{\boldsymbol{\sigma}} - \mathbf{b}'$ denotes the deviatoric driving stress, A is a constant, θ the temperature, and $\tilde{s}(\gamma^p) = s_s + (s_0 - s_s) \exp(-h\gamma^p/s_s) + \alpha p$ is the athermal yield strength which describes the characteristic intrinsic softening of glassy polymers by the decrease from the initial value s_0 to the saturation value s_s and additionally depends (via the constant α) on the hydrostatic pressure p . The back stress tensor \mathbf{b} describes progressive hardening due to molecular chain alignment at large stretches (Fig. 2). Full details of the model are given in the above literature.

Of particular importance for the competition between plastic yielding and crazing is the initial yield stress, i.e. the peak above the subsequent plateau, see Fig. 2. This peak value depends (besides the current temperature and strain rate) strongly on the thermal pre-history of the material (referred to as *physical aging*); in the constitutive model it is represented by the initial yield strength s_0 [3]. Low values of s_0 , and hence a small amount of softening correspond to a material rapidly cooled (quenched) from the melt,

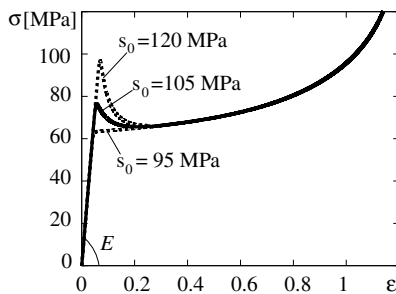


Fig. 2. Uniaxial tensile response of SAN model in terms of true stress vs. logarithmic strain in absence of crazing at constant strain rate $\dot{\epsilon} = 0.1$ / sec for different values of the initial yield strength s_0 .

while annealing (i.e. aging) leads to higher values of s_0 [8]. The range of values indicated in Fig. 2 is adopted from [7].

2.3. Cohesive surface modeling of crazing

Crazes are narrow crack-like zones in which the polymer material is drawn from the adjacent bulk into thin fibrils by which a craze (contrary to a crack) is capable of carrying stress (e.g. [8,10]). Owing to the localized nature of a craze, it may well be described by a cohesive surface model as developed, for instance, in [18,7]; this approach is adopted in the present work. A key ingredient is the relation for the craze widening rate

$$\dot{\Delta}_c = \dot{\Delta}_0 \exp \left[\frac{A_c}{\theta} (T_n - \sigma_c) \right] \quad (2)$$

which (besides the constants $\dot{\Delta}_0$, A_c and the temperature θ) depends on the normal traction T_n on the cohesive surface and the craze widening resistance (cohesive strength) σ_c . In contrast to the constant cohesive strength in previous studies [18,7], a more general dependence $\sigma_c(\Delta_c)$ on the separation (craze width) Δ_c is considered here (Fig. 1c). An initial decrease from the value σ_c^{init} down to σ_c^{min} (i.e. softening) can be motivated from the higher stress required to draw the initially thick “primary” fibrils than the thinner “mature” ones. Subsequent hardening, i.e. an increase of the cohesive strength to some value σ_c^{max} (Fig. 1c) may result from the necessary entanglement-loss when molecules coming from increasing larger distances have to be drawn into the fibrils; such a response has been predicted in a detailed micromechanical study of the fibril drawing process in [1]. Moreover, Donald et al. [6] have shown that the surface stress profile along a craze (computed from the measured craze opening profile) displays peaks at the craze tip and the crack tip; the stress profile along a craze may be taken as a record of the (local) stress history in the course of craze widening, thus motivating a non-monotonous variation of $\sigma_c(\Delta_c)$. Finally, craze breakdown (fibril rupture) takes place at a critical craze width Δ_c^{cr} (Fig. 1c). The forward gradient scheme presented in [18] for the numerical treatment of the cohesive surface model is extended here to account for the additional contribution due to $\sigma_c(\Delta_c)$. A more detailed discussion of the cohesive model and the calibration of its parameters are given in [15].

Various criteria for craze initiation in glassy polymers are suggested in the literature (e.g. [10]). Recent experiments by Saad-Gouider et al. [13] indicate that in brittle materials (e.g. polystyrene) craze initiation is controlled by the maximum principal stress whereas in more ductile materials (e.g. polycarbonate) a critical value of hydrostatic stress σ_m is more appropriate. For SAN which displays an intermediate brittleness both criteria, giving rise to different values of σ_c^{init} (Fig. 1c), are considered in the present study.

In view of the uncertainties associated with the craze response three different variations of the cohesive strength $\sigma_c(\Delta_c)$, referred

to as models #1, #2 and #3 and sketched in Fig. 1c, are investigated here. Common to all is the value $\sigma_c^{\text{min}} = 60$ MPa which is based on experiments by Donald et al. [6] on SAN, the matrix material in the present study. The critical craze width Δ_c^{cr} is taken to be 0.2 times the (fixed) rubber particle radius.

- Model #1: craze initiation at hydrostatic stress $\sigma_m^{\text{cr}} = 65$ MPa, hardening up to $\sigma_c^{\text{max}} = 100$ MPa,
- model #2: craze initiation at $\sigma_c^{\text{cr}} = 80$ MPa, hardening up to $\sigma_c^{\text{max}} = 100$ MPa,
- model #3: craze initiation at $\sigma_c^{\text{init}} = 80$ MPa, no hardening.

In model #1 the initial cohesive strength σ_c^{init} is determined from the normal traction on the cohesive surface at craze initiation; for the prescribed value of σ_m this typically leads to $\sigma_c^{\text{init}} > 100$ MPa and crazing is preceded by plastic deformation of the surrounding matrix. In contrast, for models #2 and #3 with a lower value of σ_c^{init} craze initiation takes place in the elastic range of matrix deformation.

3. Numerical results

Loading of the axisymmetric unit cell is imposed by prescribing velocities on the horizontal and vertical boundaries so that the overall stress ratio $\Sigma_{1,2}/\Sigma_3$ is kept constant. Though rate-dependence is an important issue in the behaviour of polymers, it is (for brevity) not investigated in the present work and a constant overall axial strain rate $\dot{\epsilon} = 1 \text{ sec}^{-1}$ is considered in all examples.

For the three different cohesive models, Fig. 3 shows the overall axial stress–strain response in case of a material with a void volume fraction $f_0 = 0.05$ and an initial matrix yield stress $s_0 = 110$ MPa. Under uniaxial overall loading (Fig. 3a) the locally high hydrostatic stress required to initiate crazing according to craze model #1 is attained only after some amount of plastic defor-

mation has taken place (indicated by the nonlinear response prior to the abrupt stress drop), whereas models #2 and #3 lead to crazing prior to bulk plasticity which results in smaller overall failure strains. An increase of the craze stress in the course of craze widening (#2) enforces larger elastic matrix deformation and leads to a larger failure strain than without hardening (#3). Fig. 3b shows corresponding results for a higher overall stress triaxiality where crazing according to each cohesive model takes place in the elastic range of matrix deformation; the ultimate strain at failure then is equal for models #1 and #2 since they have the same hardening behavior.

The cell model response for a lower initial matrix yield stress ($s_0 = 95$ MPa) and uniaxial overall loading is depicted in Fig. 4a. In case of a hardening craze behavior (#1 and #2) it differs fundamentally from Fig. 3a in that for model #1 crazing is completely suppressed and for model #2 (low craze initiation stress) craze widening ceases after some amount due to the increase of cohesive strength and matrix yielding sets in. This transition is illustrated in Fig. 4b showing for the cohesive model #2 the portions of stored elastic energy W_{el} , plastic matrix dissipation W_{pl} and cohesive work W_{coh} of the craze per total work W_{tot} expended to the cell in the course of overall deformation. Obviously, crazing is initially the dominant dissipative mechanism but is later exceeded by bulk plasticity. It should be mentioned that for cohesive model #3 (low initiation stress and no hardening) or for higher overall stress triaxiality (not shown here) the same results as in Fig. 3 are obtained, i.e. the response is not affected by the matrix yield stress s_0 .

So far only a rather small void volume fraction of $f_0 = 0.05$ has been considered. For the stacked particle arrangement of the present model it can be presumed that larger volume fractions lead to an amplification of the tensile stress in the particle equator region and hence promote crazing. This effect is investigated in case of the cohesive models #1 and #2 in Fig. 5 for an initial matrix yield stress $s_0 = 95$ MPa and in Fig. 6 for $s_0 = 110$ MPa. Indeed, in case

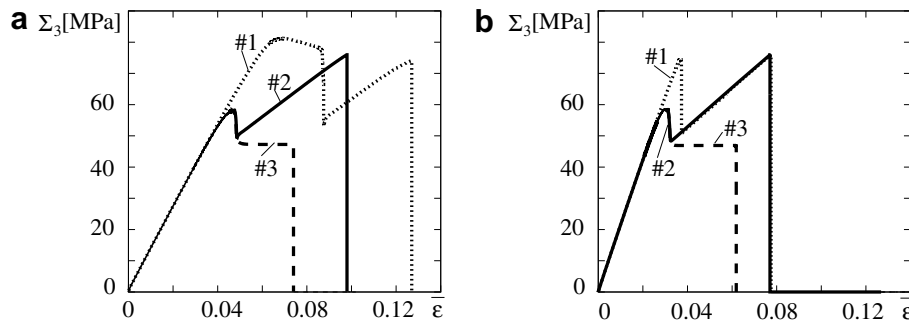


Fig. 3. Effect of craze properties under (a) uniaxial overall tension $\Sigma_1 = 0$, and (b) $\Sigma_1 = 0.5\Sigma_3$; $f_0 = 0.05$, $s_0 = 110$ MPa.

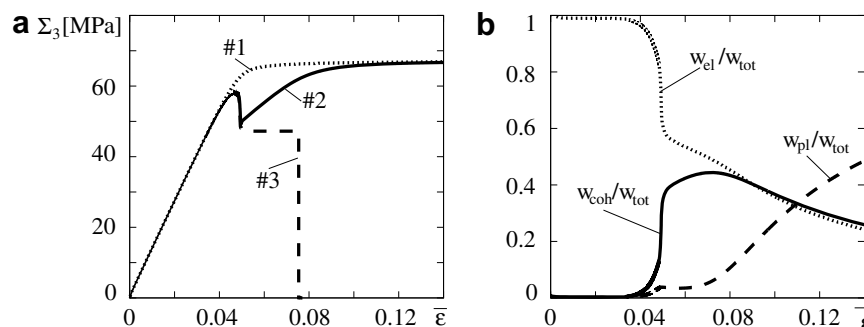


Fig. 4. (a) Effect of crazing model for uniaxial overall tension and $f_0 = 0.05$, $s_0 = 95$ MPa, and (b) variation of energy portions in case of crazing model #2.

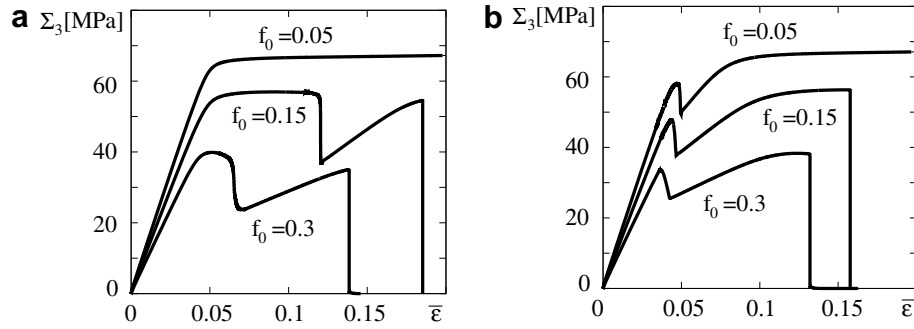


Fig. 5. Effect of rubber content (porosity) for (a) crazing model #1 and (b) crazing model #2 under uniaxial overall tension and initial matrix yield stress $s_0 = 95$ MPa.

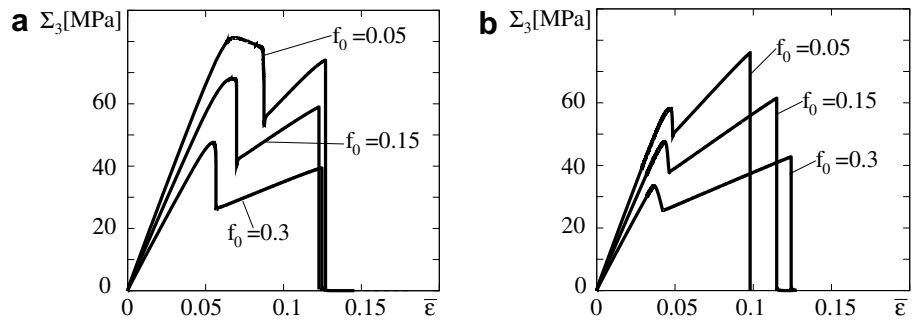


Fig. 6. Effect of rubber content (porosity) for (a) crazing model #1 and (b) crazing model #2 under uniaxial overall tension and initial matrix yield stress $s_0 = 110$ MPa.

of a low matrix yield stress, where for $f_0 = 0.05$ crazing does not occur at all (Fig. 5a) or comes to an arrest (Fig. 5b), an increase of f_0 leads to a decrease of the failure strain. However, for a high matrix yield stress ($s_0 = 110$ MPa) the amount of matrix plasticity prior to crazing that occurs in case of cohesive model #1 decreases with increasing f_0 which leads to almost equal failure strains (Fig. 6a). Moreover, in case of cohesive model #2 the purely elastic matrix behavior observed for $f_0 = 0.05$ also prevails for larger volume fractions; as a consequence, the overall failure strain then increases with increasing f_0 (Fig. 6b).

4. Discussion and conclusions

In this study the influence of some key material and microstructural parameters on the interaction between crazing and matrix yielding in rubber-toughened glassy polymers (in particular ABS) has been investigated. It turns out that, depending on the combination of these parameters, the overall response of the material (e.g. failure strain) may differ significantly. The present findings indicate that without a hardening craze behavior (model #3) or for high triaxiality loading, matrix yielding does not occur and that a larger rubber content f_0 promotes crazing. Moreover, the dependence of the overall strain at failure on the rubber content may be strongly affected by the matrix yield behavior, as can be seen by comparing Figs. 5b and 6b. However, these observations have to be taken with some caution; they are partly artifacts of the simple stacked morphology considered here. More realistic microstructures, allowing for more complex void/craze interaction such as mutual shielding, see [14], therefore need to be investigated and are subject of ongoing research.

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