Multi-scale Mechanical Model for predicting Fracture Initiation in Strain-Crystallizing Rubbers

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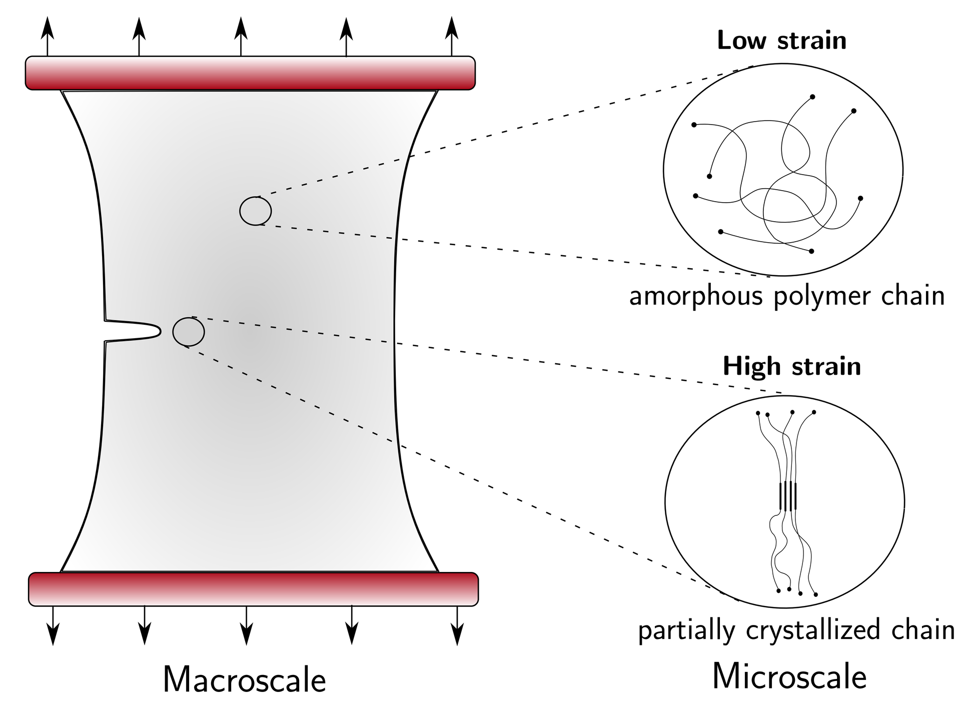
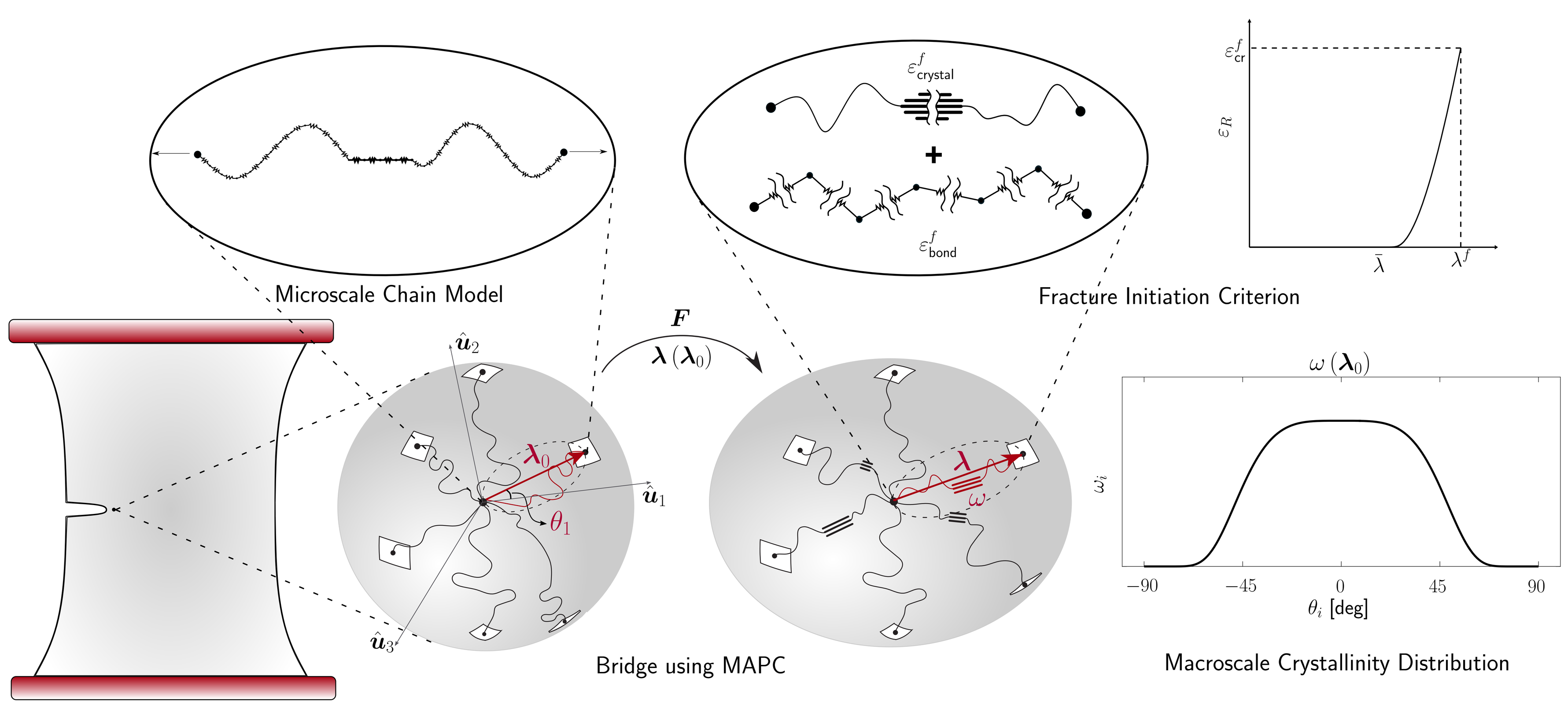
Introduction

Rubber-based materials find a myriad of applications in epidermal electronics, self-actuators, implantable sensors etc. due to their desirable properties like high stretchability, high toughness, small modulus and low cost. Certain rubbers, like Natural Rubber (NR), have been found to exhibit a multi-scale phenomenon called Strain-Induced Crystallization (SIC) which reinforces against fracture.



SIC has been found to be exhibited by only certain polymers having segments of macromolecules with mutually conforming structure. Thermodynamically, the phase transition from amorphous to crystalline phase is governed by the latent heat of fusion and entropy change.

Multi-scale Model Overview



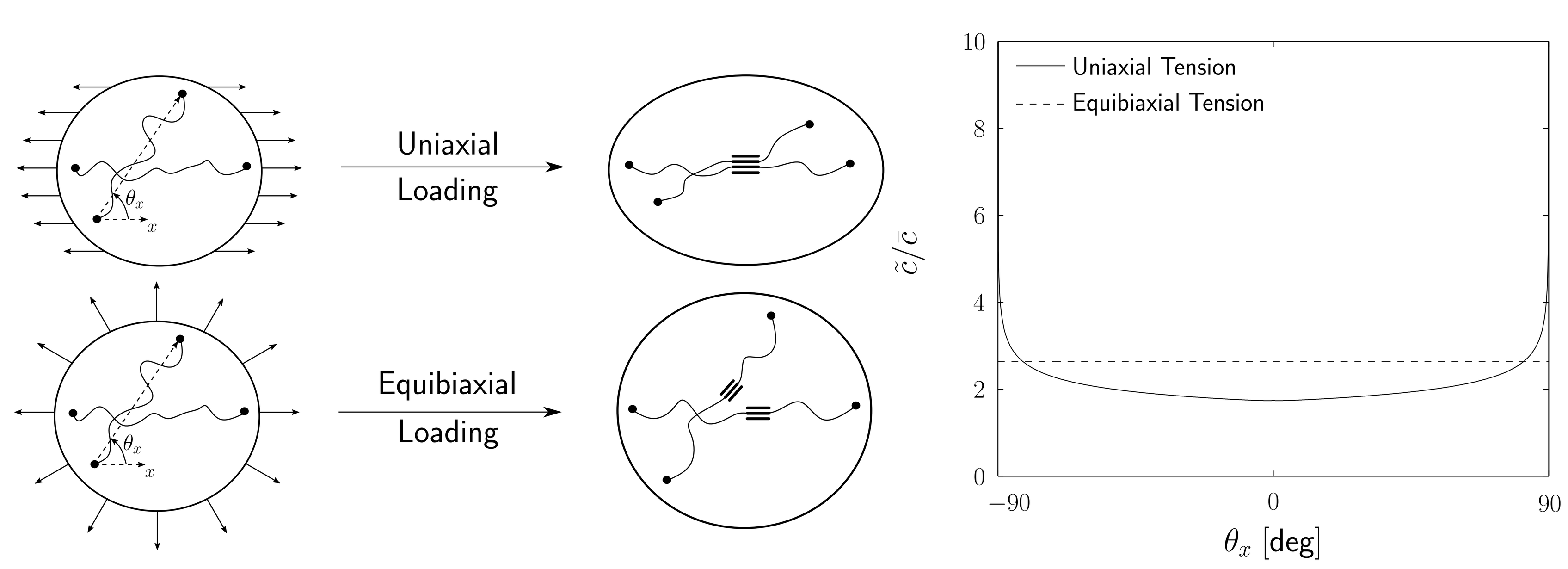
Microscale Chain Model

Langevin statistics is used for modeling the amorphous chains which are assumed to be made up of a number of elastic chain segments. The extensibility in the chain segments is due to the deformation of the constituent molecular bonds [1,2]. The free energy expression is given by

$$\bar{\psi}(\lambda,\omega,\lambda_b) = \underbrace{nN\varepsilon_b(\lambda_b)}_{\text{Bond Stretch}} + \underbrace{\mu N(1-\omega)\left[\beta\Lambda + \ln\frac{\beta}{\sinh\beta}\right]}_{\text{Amorphous}} + \underbrace{\tilde{c}\omega - \xi\left(\frac{\omega}{\omega_{max}} + \ln(1-\frac{\omega}{\omega_{max}})\right)}_{\text{Crystalline}}$$

Degree of crystallization ω in chain and bond stretch λ_b in chain segments are governed by

$$\dot{\omega} = -q\frac{\partial\psi}{\partial\omega} \quad \text{and} \quad \frac{\partial\bar{\psi}}{\partial\lambda_b} = 0$$



Nucleation barrier $\tilde{c}$ is considered to be function of applied loading and initial chain orientations [3]

$$\tilde{c}\,(\chi,\hat{\boldsymbol{v}},\boldsymbol{\lambda}_0) = \frac{\bar{c}}{\left[\sum_{i=1}^{3}\chi_i^2\left(\sin^{-1}|\,\hat{\boldsymbol{v}}_i\cdot\boldsymbol{\lambda}_0\,|\right)^{\chi_2/\chi_1} + \gamma\right]^{p_c}}$$

Bridge using MAPC

Stretch $\boldsymbol{\lambda}$ in each chain is obtained using free energy minimization of the system satisfying the Maximal Advance Path Constraint (MAPC) [4] as

$$\underset{\boldsymbol{\lambda}}{\text{Minimize}}\ \langle\bar{\psi}\rangle \ \text{subject to}\ \langle\boldsymbol{\lambda}\otimes\boldsymbol{\lambda}_0\rangle = \frac{1}{3}\bar{\boldsymbol{F}}$$

This accounts for non-affine, anisotropic deformations; hence advantageous for fracture applications.

Macroscale Crystallinity Distribution

A crystallinity distribution [5] using parameters $\boldsymbol{\Omega}_i = [\phi_{1i},\phi_{2i},a_i,b_i]$ centered around axes $\{\hat{\boldsymbol{u}}_1,\hat{\boldsymbol{u}}_2,\hat{\boldsymbol{u}}_3\}$ is given by

$$\omega = \sum_{i=1}^{3}\chi_i\,\hat{\omega}_i = \sum_{i=1}^{3}\chi_i\,a_i\exp\left(-b_i(\ln\cos\theta_i)^2\right) \quad \text{with} \quad \cos\theta_i = |\hat{\boldsymbol{u}}_i\cdot\boldsymbol{\lambda}_0|$$

Distribution parameters are fit using least squared minimization of error between apparent crystallinity rate $\dot{\tilde{\omega}}$ using this distribution and the actual chain crystallinity rate $\dot{\omega}$.

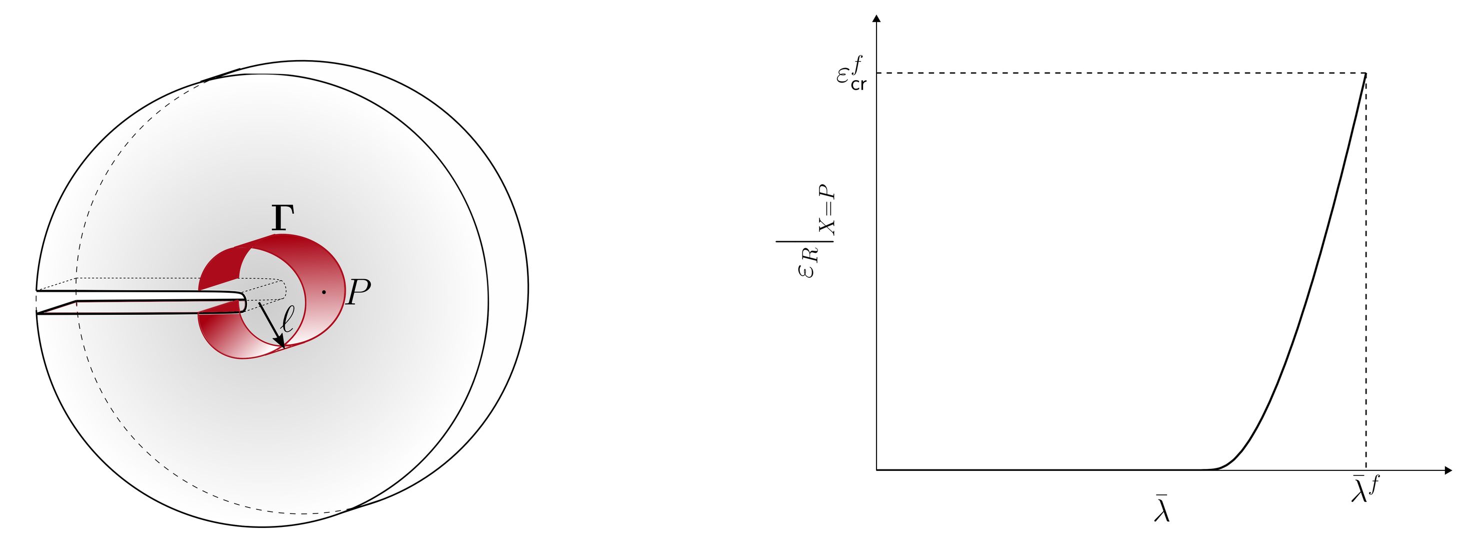
Fracture Initiation Criterion

Critical internal energy required to break the crystallite $\varepsilon^f_{\text{crystal}}$ is empirically assumed based on that for the elastic bonds $\varepsilon^f_{\text{bond}}$. Total effective critical energy is postulated as

$$\varepsilon^f_{\text{cr,eff}} = \varepsilon^f_{\text{bond}} + \varepsilon^f_{\text{crystal}} = nN\varepsilon^f_b + \frac{\omega}{1-\omega}\varepsilon^f_{\text{bond}} = \frac{nN\varepsilon^f_b}{1-\omega} = \frac{\varepsilon^f_{\text{cr}}}{1-\omega}$$

Internal energy for rupture is postulated as

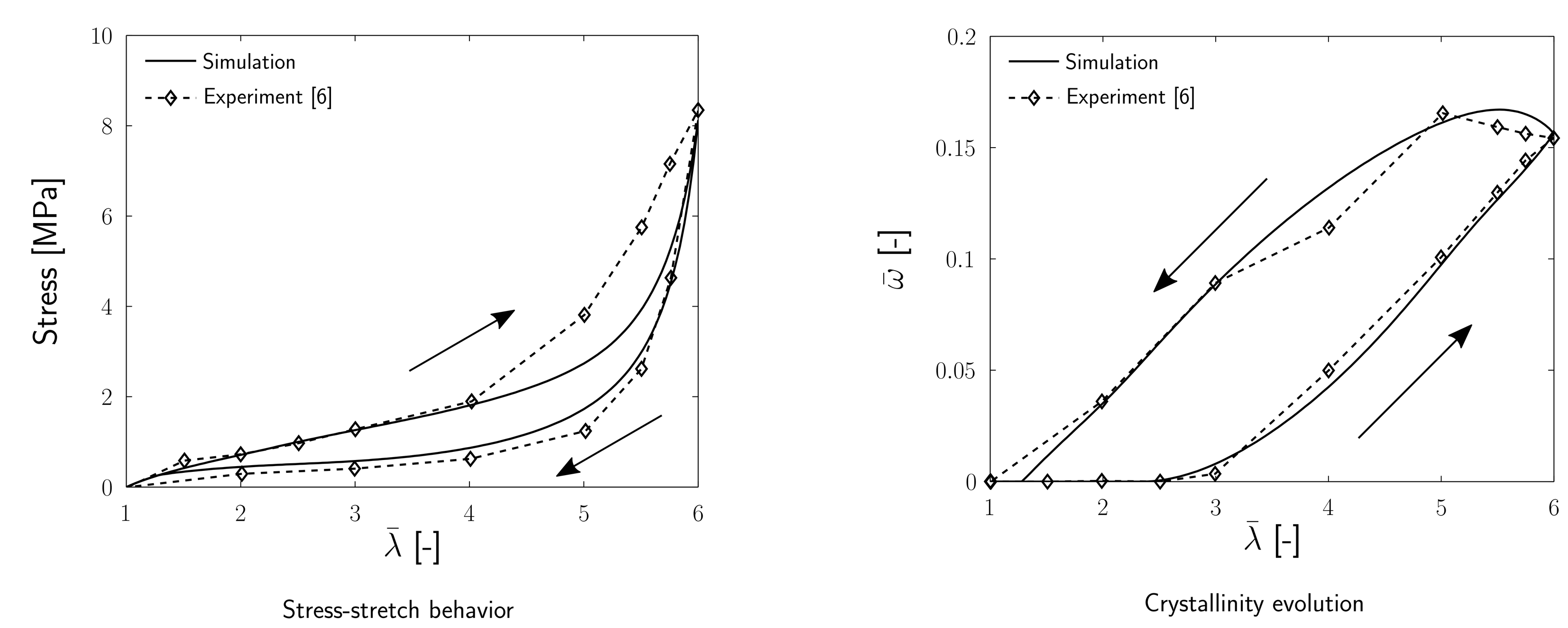
$$\varepsilon_R = \max_{l=1,\ldots,n_{\text{int}}} nN\varepsilon_b(\lambda_{b,l})(1-\omega_l)$$



This internal energy to rupture is checked at various points $X = P$ on surface $\boldsymbol{\Gamma}$ for criterion

$$\varepsilon_R\big|_{X=P} = \varepsilon^f_{\text{cr}} \implies \text{fracture initiation}$$

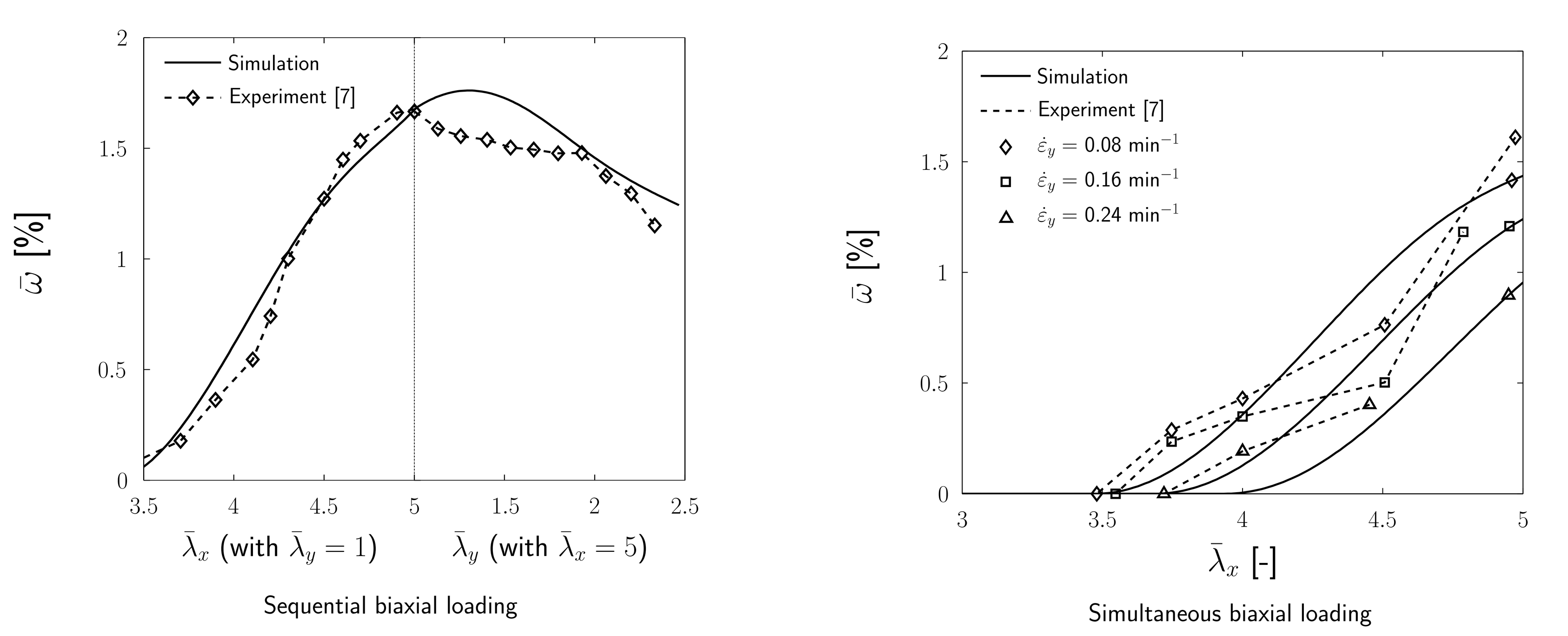
Results - Homogeneous Uniaxial Test Material Behavior



Stress-stretch behavior   Crystallinity evolution

Our model successfully captures the hysteresis behavior in both stress and crystallinity.

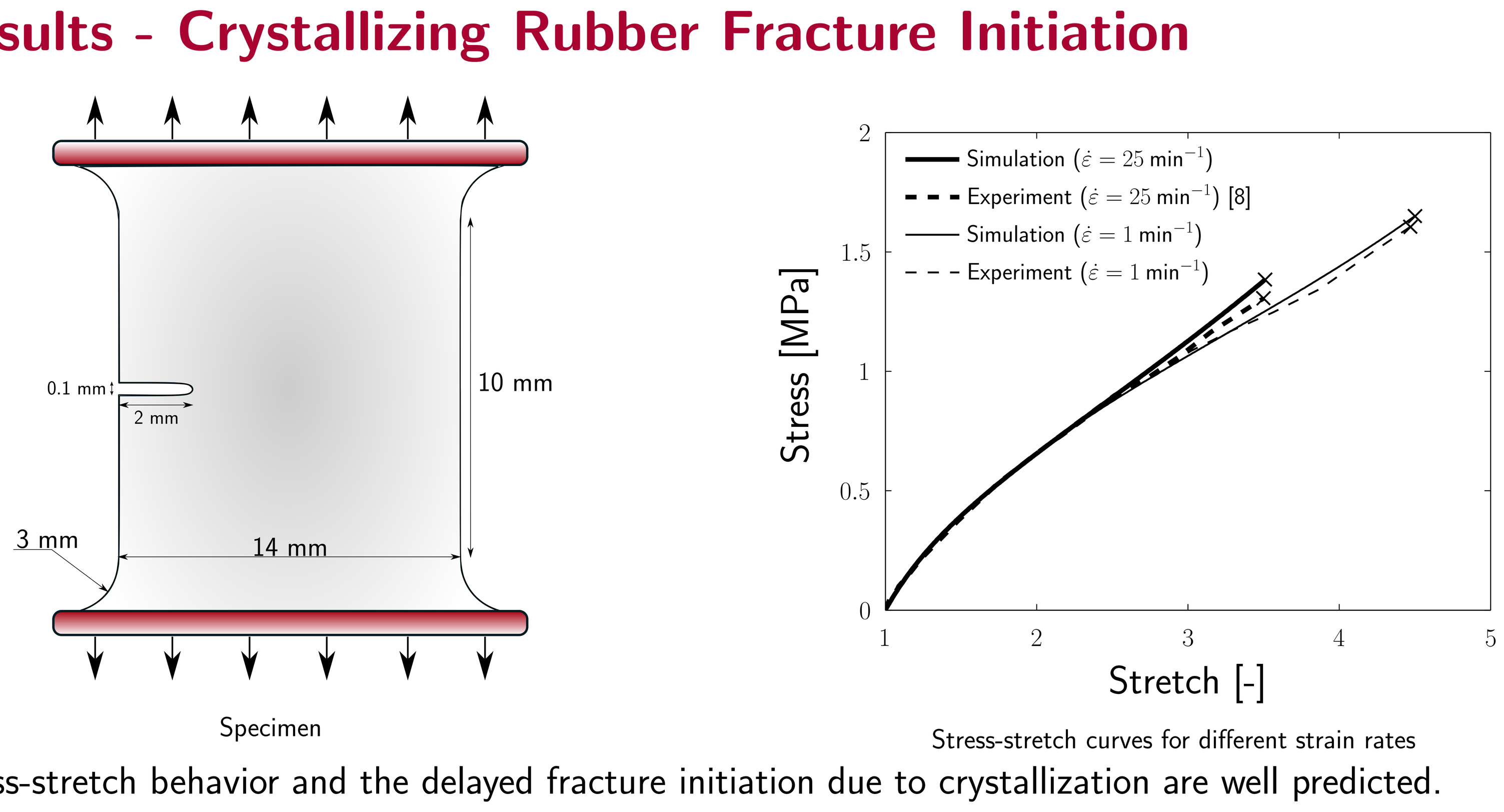
Results - Biaxial Test Material Behavior



Sequential biaxial loading   Simultaneous biaxial loading

Our model successfully captures the frustration in crystallinity due to biaxial loading. Considering the effect of loading and chain orientation on the nucleation barrier is mainly responsible for this.

Results - Crystallizing Rubber Fracture Initiation



Specimen   Stress-stretch curves for different strain rates

Stress-stretch behavior and the delayed fracture initiation due to crystallization are well predicted.

References

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