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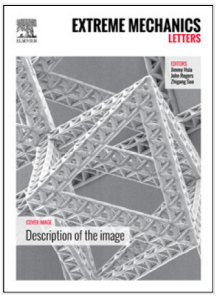

Rupture of polymers by chain scission

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Rupture of polymers by chain scission

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Abstract

One of the distinguishing features of elastomeric materials, which consist of a network of flexible polymeric chains, is that the deformation response is dominated by changes in entropy. Accordingly, most classical theories of rubber-like elasticity consider only the entropy and neglect any changes in internal energy. On the other hand, the fracture of strongly cross-linked elastomers is essentially energy dominated, as argued in the well-known Lake-Thomas model for the toughness of elastomers. However, a single model unifying these two phenomena is still lacking. We provide a rational yet simple model for deformation and fracture of cross-linked polymers, based on two ingredients: (i) a non-Gaussian statistical mechanics model of polymer chains that accounts for the increase in energy due to the deformation of molecular bonds; (ii) a chain scission criterion based on the bond deformation energy attaining a critical value. Using this model, we can estimate the rupture stretch of elastomeric materials from fundamental quantities describing the polymer network. We use this model to relate the flaw sensitivity of elastomers to an intrinsic material length scale related to the network structure.

Keywords: elastomer; deformation; fracture; scission

1 Introduction

The classical statistical mechanical model of Kuhn and Grün [1] for the deformation response of a single polymer chain is based on the assumption that the change in free energy upon stretching of a long-chain molecule is dominated by the change in configurational entropy, and that any change in internal energy is negligible. A key feature of this model is that it accounts for the finite extensibility of the chain and reproduces the experimentally observed stiffening of the chain as it is highly stretched. This theory is the basis of a number of notable models for the deformation response of polymeric networks (see [2, 3] and the references therein). On the other hand, the fracture behavior of polymers is widely accepted to be adequately described by the model of Lake and Thomas [4], which connects the macroscopic work of fracture (the critical energy release rate G_c) to the energy required to strain and ultimately rupture bonds between monomer units. According to the arguments of Lake and Thomas, the *entropic* contribution to the free energy is negligible at the point of rupture, and the internal energy due to the bond deformation dominates. How can these models—both well accepted—be reconciled? The goal of this letter is to address this question.

The plan of this letter is as follows. In Section 2, we modify the single chain model of Kuhn and Grün to include an internal energy contribution which we associate with the mechanism of stretching of molecular bonds. In light of the success of the classic freely jointed chain model, any new model should behave similarly at stretch levels below rupture. On the other hand, to be consistent with the arguments of Lake and Thomas, a model should also be able to predict the increase of the internal energy during deformation and describe how it ultimately comes to dominate the free energy at large stretches. Our model satisfies these objectives