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Progressive damage and rupture in polymers

Brandon Talamini, Yunwei Mao, Lallit Anand*

Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA, 02139, USA

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ABSTRACT

Progressive damage, which eventually leads to failure, is ubiquitous in biological and synthetic polymers. The simplest case to consider is that of elastomeric materials which can undergo large reversible deformations with negligible rate dependence. In this paper we develop a theory for modeling progressive damage and rupture of such materials. We extend the phase-field method, which is widely used to describe the damage and fracture of brittle materials, to elastomeric materials undergoing large deformations. A central feature of our theory is the recognition that the free energy of elastomers is not entirely entropic in nature — there is also an energetic contribution from the deformation of the bonds in the chains. It is the energetic part in the free energy which is the driving force for progressive damage and fracture.

1. Introduction

The development soft materials for mechanical applications has ushered a recent revolution in materials. Applications often depend on the great extensibility of polymer-based materials, as well as many other useful properties that soft materials can possess, including bio-compatibility, self-healing (Cordier et al., 2008; Holten-Andersen et al., 2010), and novel actuation mechanisms and functions (Tokarev and Minko, 2009). In addition to the traditional engineering uses of elastomeric materials, transformative applications are being developed daily, from surgical adhesives to replace sutures (Duarte et al., 2012), hydrogel scaffolding for tissue engineering (Lee and Mooney, 2001), and artificial cartilage, tendons and ligaments for joint repair therapies (Azuma et al., 2006; Nonoyama et al., 2016). The mechanical demands of these applications places new importance on understanding and modeling of damage and failure of these materials.

Modeling of failure in polymers falls in two broad categories: the first comprises macroscopic “top-down” approaches based on a Griffith-type critical energy release rate criterion. The application of top-down approaches to polymer fracture dates back to Rivlin and Thomas’s work with commercial rubbers (Rivlin and Thomas, 1952). The second category comprises “bottom-up” approaches that investigate the mechanisms of damage at the molecular scale and attempt to build a consistent picture up through larger scales. The second approach has been largely driven by research on biological materials and design of bio-inspired composites (see, e.g., (Baer et al., 1987; Buehler, 2006; Gao, 2006; Jackson et al., 1988; Kamat et al., 2000; Sen and Buehler, 2011; Sun and Bhushan, 2012)). An early attempt at linking these approaches occurs in the landmark paper of Lake and Thomas (1967) in which they proposed a scaling law for the critical energy release rate in terms of microscopic parameters, including the binding energy between monomer units and the chain network mesh size.

One important advantage of the bottom-up approach is the understanding that it provides on the sensitivity of materials to flaws at small length scales. The theory of Griffith governs fracture at the macro-scale, and reveals that the resistance

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* Corresponding author.
E-mail address: anand@mit.edu (L. Anand).

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of a body to fracture depends sensitively on the size of flaws contained within it (Griffith, 1921). However, the picture is different at very small length scales, since the assumption that the behavior of the crack tip region can be separated from the far-field response, which underpins the Griffith theory, does not hold. Instead, the nonlinear mechanical response of the molecular bonds is felt over the entire body (Buehler et al., 2003), and a large fraction of the material is stressed to levels approaching the ideal strength, rather than just the region near the flaw tip. As a result, the material is much less sensitive to flaws (Chen et al., 2016; Gao et al., 2003; Mao et al., 2017b). The molecular-scale physics is necessary to explain this flaw-insensitive behavior, and bottom-up modeling is necessary to control it and exploit it.

Most of the developments in the bottom-up description of failure in polymers have been conducted through the framework of molecular dynamics (see, e.g., Rottler et al., 2002; Rottler and Robbins, 2003). Unfortunately, the computational demands of molecular dynamics limit the simulated length scales and time durations to scales below those needed for engineering design and optimization. It seems likely that continuum-based approaches will be needed for these purposes for the foreseeable future. Of course, to make a predictive continuum-level model, the underlying molecular physics must be retained to the furthest extent possible. The aim of this paper is to take a step in this direction.

The simplest polymers are elastomeric materials, which consist of a chemically crosslinked network of flexible polymeric chains that can undergo large reversible deformations with negligible rate-dependence. In this paper we develop a continuum theory for modeling progressive damage and rupture of such materials. One of the distinguishing features of elastomers is that their deformation response is dominated by changes in entropy. Accordingly, most classical theories of rubber elasticity consider only changes in entropy due to deformation, and neglect any changes in internal energy (e.g., Kuhn and Grün, 1942; Treloar, 1975; Arruda and Boyce, 1993). On the other hand, as recognized by Lake and Thomas (1967), rupture is an *energetic* process at the micro-scale, emanating from the scission of molecular bonds in the polymer chains.[1] In order to achieve the microscopic perspective, our theory incorporates a recently proposed hyperelastic model that describes both the entropic elasticity of polymer chains, as well as a description of the mechanics of the molecular bonds in the backbone of the chain (Mao et al., 2017b).

We make use of a phase-field approach to model the loss of stress-bearing capacity of the material due to the softening and rupture of bonds at large stretches. The model describes damage initiation, propagation, and full rupture in polymeric materials. The phase-field acts as a damage variable, with a nonlocal contribution to the free energy that regularizes the theory and sets a length scale for the rupture process.

In its structure, our framework is similar to the top-down phase-field approaches to fracture based on Bourdin et al. (2000) that have become popular over the last 20 years, including several devoted to rupture of elastomeric materials (Miehe and Schänzel, 2014; Raina and Miehe, 2016; Wu et al., 2016). The distinction of our model is in the scale: in the previous works, the phase-field serves as mathematical regularization of the critical energy release rate theory — thus embodying a macroscopic approach — while here we directly consider the physics of bond scission at the local scale. In particular, our work significantly departs from these previous works in the definition of the driving force for damage. The proposed model discriminates between entropic contributions to the free energy due to the configurational entropy of the polymer chains, and the internal energy contributions due to bond deformation. We argue that the evolution of the phase-field should be driven solely by the internal energy, since the microscopic bond scission mechanism it represents is fundamentally an energetic process.

The plan of this paper is as follows. In Section 2 we give a brief summary of the structure of the theory, including the balance laws and the constitutive framework. In Section 3 we specify the constitutive relations of the theory. We proceed step-by-step in the development of the constitutive relations, starting with the deformation response of a single chain with no damage, then proceed to a damage model for softening and scission of a single chain. We discuss how these specific constitutive relations represent a microscopic view of damage in elastomers. Next, we generalize the single chain model to describe the response of bulk material comprised of a network of chains, which bridges the microscopic perspective to the macroscopic one. In Section 5 we study the capability of the model to describe flaw-size sensitivity in single-edge-notched specimens which are sub-millimeter in size, with micron-dimensioned cracks. In Section 6 we show the capability of the theory and numerical simulation capability to model the experimental results of Hocine et al. (2002) on fracture of double-edge-notched specimens of a styrene-butadiene elastomer (SBR) — specimens which are tens of millimeters in size, with millimeter-dimensioned cracks. Finally, we summarize the main conclusions and make some final remarks in Section 7. A full derivation of the balance laws using the principle of virtual power and the development of the thermodynamically consistent constitutive framework are included in Appendix A, and some details of the numerical implementation of the theory are given in Appendix B.

2. Summary of the constitutive theory, governing partial differential equations and boundary conditions

We have formulated a phase-field/gradient-damage theory for fracture of a finitely-deforming elastic solid using the pioneering virtual-power approach of Gurtin (1996, 2002). This approach leads to “macroforce” and “microforce” bal-

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[1] If the cross-linking chemical bonds in an elastomeric network are strong, then fracture is expected to occur by scission of the chains between the crosslinks, as envisioned in the classical model of Lake and Thomas (1967), while if the chemical crosslinks are weak then fracture is expected to occur because of the scission of the cross-linking bonds themselves. In this paper we focus our attention on networks with strong cross-linking bonds which fail by chain-scission.