

Contents lists available at [ScienceDirect](http://www.sciencedirect.com)

Journal of the Mechanics and Physics of Solids

journal homepage: www.elsevier.com/locate/jmps

Mechanics of mechanochemically responsive elastomers

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ARTICLE INFO

Article history:

Received 23 January 2015

Received in revised form

15 April 2015

Accepted 15 May 2015

Available online 27 May 2015

Keywords:

Mechanochemistry

Stimuli-responsive polymer

Spiropyran

Constitutive model

Interpenetrating-network model

Chain-length distribution

ABSTRACT

Mechanochemically responsive (MCR) polymers have been synthesized by incorporating mechanophores – molecules whose chemical reactions are triggered by mechanical force – into conventional polymer networks. Deformation of the MCR polymers applies force on the mechanophores and triggers their reactions, which manifest as phenomena such as changing colors, varying fluorescence and releasing molecules. While the activation of most existing MCR polymers requires irreversible plastic deformation or fracture of the polymers, we covalently coupled mechanophores into the backbone chains of elastomer networks, achieving MCR elastomers that can be repeatedly activated over multiple cycles of large and reversible deformations. This paper reports a microphysical model of MCR elastomers, which quantitatively captures the interplay between the macroscopic deformation of the MCR elastomers and the reversible activation of mechanophores on polymer chains with non-uniform lengths. Our model consistently predicts both the stress–strain behaviors and the color or fluorescence variation of the MCR elastomers under large deformations. We quantitatively explain that MCR elastomers with time-independent stress–strain behaviors can give time-dependent variation of color or fluorescence due to the kinetics of mechanophore activation and that MCR elastomers with different chain-length distributions can exhibit similar stress–strain behaviors but very different colors or fluorescence. Implementing the model into ABAQUS subroutine further demonstrates our model's capability in guiding the design of MCR elastomeric devices for applications such as large-strain imaging and color and fluorescence displays.

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1. Introduction

Polymers capable of chemical reactions in response to external mechanical stimuli offer great promise for developing future sensors, memories, displays and photomodulators (Beyer and Clausen-Schaumann, 2005; Caruso et al., 2009; Sagara and Kato, 2009). Recent years, a novel strategy for fabricating mechanochemically responsive (MCR) polymers has been developed by covalently incorporating molecules capable of force-triggered chemical reactions, or so-called mechanophores, into polymer networks (Beyer and Clausen-Schaumann, 2005; Black et al., 2011a; Caruso et al., 2009; Kean and

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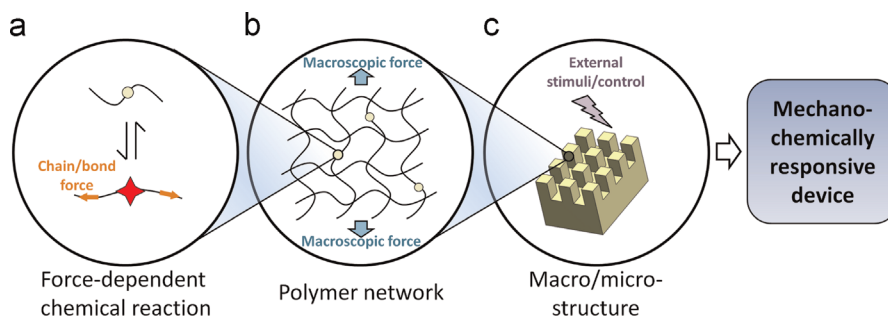


Fig. 1. Three levels of designs for the mechanochemically responsive devices. (a) On the molecular level, the development and optimization of new mechanophores capable of force-dependent chemical reactions. (b) On the network level, designing the architectures of polymer networks, on which mechanophores are coupled. (c) On the device level, designing structures and actuation mechanisms of the devices.

Craig, 2012). Deformation of MCR polymers stretches polymer chains which apply forces on the mechanophores and triggers their reactions, leading to phenomena such as changing colors, varying fluorescence and releasing molecules of the MCR polymers. The working mechanism of MCR polymers motivates material design on three levels (Fig. 1): (1) On the molecular level, various mechanophores are synthesized for force-dependent chemical reactions, giving externally detectable chemical or optical signals (Fig. 1a) (Beyer and Clausen-Schaumann, 2005; Black et al., 2011a; Caruso et al., 2009; Kean and Craig, 2012). (2) On the network level, to control the forces applied on mechanophores, the mechanophore-bearing polymer chains can be crosslinked into different network architectures, upon which the macroscopic deformation will be applied (Fig. 1b) (Beiermann et al., 2014; Kingsbury et al., 2011; Lee et al., 2013). (3) On the structure level, to control the macroscopic deformations, the MCR polymers are tailored into various designed structures, which can be deformed by external stimuli such as applied forces, swelling, electric and magnetic fields (Fig. 1c) (Caruso et al., 2009; Lee et al., 2014; Q. Wang et al., 2014). Through the three-level designs, the MCR polymers have been assembled into functional MCR devices for applications as diverse as controlled color display, fluorescence emission, release of catalysts and small molecules, and constructive network remodeling (Chen et al., 2012; Davis et al., 2009; Hickenboth et al., 2007; Lenhardt et al., 2010; Ramirez et al., 2013).

During the design of MCR devices, it is highly desirable that the MCR polymers can be reversibly and repeatedly activated and deactivated. However, most existing MCR polymers are in glassy or semicrystalline states, whose activation requires irreversible plastic deformation or fracture of the polymers. As a result, these MCR polymers cannot fully recover their initial shapes after the first activation, and therefore cannot be activated reversibly or repeatedly (Black et al., 2011b; Chen et al., 2014; Davis et al., 2009; Ducrot et al., 2014; Lee et al., 2013, 2010; Lenhardt et al., 2011; O'Bryan et al., 2010). While mechanophores have been incorporated into thermoplastic elastomers (Beiermann et al., 2014; Chen et al., 2014; Davis et al., 2009; Larsen and Boydston, 2014; Lee et al., 2010; Zhang et al., 2014), little success has yet been achieved to activate the MCR polymer repeatedly to fully recover its initial shape at the room temperature.

Recently, we developed new MCR elastomers by covalently coupling spiropyrans (Davis et al., 2009) – mechanophores that can change color and fluorescence under sufficiently high forces – into the backbone chains of a highly stretchable elastomer network, polydimethylsiloxane (PDMS) Sylgard 184 (Gossweiler et al., 2014; Q. Wang et al., 2014). The MCR elastomers can recover their initial shapes under multiple cycles of large deformation, allowing for reversible and repeated variations of the color and fluorescence of the elastomers on demand. The MCR elastomers can also be assembled into devices such as a display that is remotely controlled by external physical stimuli (e.g., electric fields) to generate on-demand fluorescent and color patterns. These MCR elastomer systems open promising venues for creating flexible MCR devices with diverse applications in flexible displays, optoelectronics, biomedical luminescent devices and dynamics camouflage skins (Q. Wang et al., 2014). Despite the potential, the microscopic mechanical details underlying the performance of the MCR elastomers have yet to be investigated, and those mechanistic insights might enable the optimization of MCR elastomer response. For example, the relationship between the macroscopic deformation of the MCR elastomers, the distribution of polymer chain lengths in the network, and the extent of activation of mechanophores embedded along those polymer chains are not understood. These understandings, if achieved, might help guide the development of MCR elastomers, and improve the design of various MCR-elastomer devices (Fig. 1). Recently, Silberstein et al. (2014, 2013) developed the first multiscale framework aimed at understanding the activation of mechanophores within the glassy matrix and viscous rubbery networks. These models probe activation modes that are coupled to irreversible deformation of MCR polymers, and they do not capture the activation within overstressed but elastic, reversible systems. In addition, they do not account for the effect of polymer-chain-length inhomogeneity on mechanophore activations.

In this paper, we report a microphysical model of MCR elastomers, which can quantitatively characterize the process that the macroscopic deformation of the MCR elastomers reversibly activates microscopic mechanophores on polymer chains with intrinsically non-uniform lengths (Erman and Mark, 1997; Flory, 1953; Mark, 1999; Rubinstein and Colby, 2003; Treloar, 1975). We model the MCR elastomer as an interpenetrating network composed of polymer chains with different lengths of defined distributions. Therefore, the same macroscopic deformation of the elastomer will induce different microscopic

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