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Modeling mechanophore activation within a viscous rubbery network



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ABSTRACT

Mechanically induced chemical reactivity is a promising means for designing self-sensing and autonomous materials. Force sensitive chemical groups called mechanophores can be covalently linked into polymers in order to trigger specific chemical reactions upon mechanical loading. A model framework is developed to describe the response of these mechanophores to mechanical loading within an elastomeric matrix. A multiscale modeling scheme is used to couple mechanophore kinetics with rubbery elasticity. In particular, transition state theory for the population of mechanophores is modified to account for the stress-induced changes in kinetics within the solid state. The model is specified to the case of spiropyran covalently linked into a polymethacrylate (PMA) backbone. This optically trackable mechanophore (optically active through absorption and fluorescence when triggered) allows the model to be assessed in comparison to observed experimental behavior. The activation predicted by the ideal viscous elastomer model is reasonable, but consistently occurs at a larger strain than in the experiments. The glassy portion of the PMA response accounts for part of the difference in the onset of activation between experiments and the ideal elastomer model. The glassy stress response is therefore included as an additional empirically determined driving force for activation in the model. The remainder of the discrepancy between the experimental and simulation results is attributed to force inhomogeneity within the rubbery network, highlighting that the mechanophore response is correlated with local force history rather than with macroscopic stress.

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1. Background

Mechanically sensitive molecular units called mechanophores can be covalently linked into polymers in order to trigger specific chemical reactions upon mechanical loading. Mechanophores present a novel means for designing multifunctional and smart materials. Efficient transmission of stress on the macroscale to force on the molecular scale results in mechanophore reactions. Mechanophores have been incorporated in a range of polymer matrices and activated under different modes of macroscopic deformation (e.g. Hickenboth et al., 2007; Caruso et al., 2009; Davis et al., 2009; Lee et al., 2010; Black et al., 2011; Beiermann et al., 2011; Kingsbury et al., 2011). In particular, the rate dependent behavior of spiropyran within linear polymethacrylate (PMA) has

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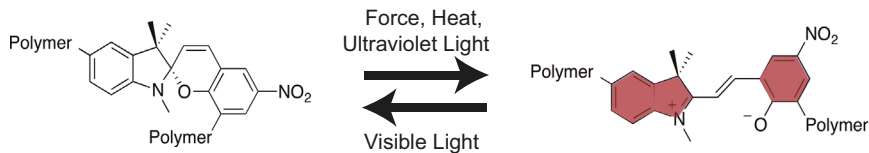


Fig. 1. Ring opening of the spiropyran mechanophore can be induced by force applied at the indicated polymer linkage points, converting the mechanophore to the merocyanine form which has a fluorescent signature. The ring opening can also be induced by exposure to ultraviolet light (~ 365 nm) or heat and reversed by exposure to visible light (~ 532 nm).

been extensively investigated. When spiropyran (SP) is linked into a polymer chain, it will transform with applied force to its merocyanine (MC) form via a ring opening reaction (Fig. 1). The state of this mechanophore is optically trackable due to a visible range fluorescence signal present in the MC form, but not detectable in the SP form. Prior results have shown that the mechanically driven conversion rate of SP to MC within PMA is dependent on stretch, orientation, stretch rate, and stretch history (Davis et al., 2009; Beiermann et al., 2011, 2012, in press). The mechanophore can also be driven from SP to MC with exposure to ultraviolet light (UV, ~ 365 nm) or heat and driven from MC to SP with visible light (~ 532 nm) (Minkin, 2004).

Here a microstructurally based model is developed to describe the response of mechanophores within solid state bulk elastomers. The model is developed with two broad targets in mind: (1) designing mechanophore-linked polymers to activate under predefined conditions, and (2) using optically trackable mechanophores to better understand force distribution within polymers. PMA is chosen as the host polymer because it is the simplest material for which data exists to benchmark the model. The model integrates results from steered molecular dynamics simulations on the mechanophore together with rubber elasticity theory.

2. Model theory

Mechanophore response within a bulk polymer depends on both the force-dependent rate kinetics of the mechanophore and the rate dependent mechanical behavior of the host polymer. The mechanophore response function and the host polymer response function must be decoupled in order for either of the model targets to be reached. A general model for each of these functions is presented below.

2.1. Mechanophore kinetics

Mechanophore level kinetics are determined using first principles methods that incorporate external force pulling schemes. Ab initio steered molecular dynamics (AISMD) enables predictions of mechanophore reactivity in response to an applied force (Ong et al., 2009). This method employs a constant force scheme whereby applied force is directed to select atomic sites on the mechanophore, consistent with the polymer chain connection points. The AISMD simulations dynamically solve the electronic Schrödinger equation along with the Newtonian dynamics of the atoms, allowing arbitrary rearrangement of covalent bonds. The method has the important attribute of requiring no fitting parameters, but is computationally expensive. AISMD provides information on the reaction mechanism at large forces where the simulations may span from femtosecond to picosecond time scales. To circumvent the cost of running AISMD simulations at experimentally accessible lower forces and longer timescales, a force modified potential energy surface (FMPES) framework is adopted (Ong et al., 2009). The FMPES framework provides knowledge of the minimal energy pathway (MEP) on the potential energy surface, which contains structural information regarding the reactants, transition states, and products. The MEP, which connects the minima to a transition state, can then be optimized for a given external force, providing information on the force perturbed molecular conformations. Additionally, knowledge of the activation barriers as a function of force is obtained along the reaction pathway. Since the MEP along the FMPES provides geometrical information (reactants, transition state), any single bond distance or angle can be monitored along the reaction coordinate. The attempt frequencies for the forward (activation) and reverse (deactivation) reactions can also be determined by using statistical theories, e.g. transition state theory, within the FMPES framework (Fig. 2).

Transition state theory is used to calculate reaction rates that are relevant to laboratory timescales from known force dependent activation barriers and attempt frequencies. A single reactant to single product mechanophore transformation is described by

$$\dot{\alpha} = k_f(1 - \alpha) - k_r\alpha, \quad (1)$$

where α is the concentration of mechanophores in the activated (triggered) state, \dot{x} indicates a time rate of change for variable x , k_f is the forward reaction rate, and k_r is the reverse reaction rate. In the case of the mechanophore used here there are two different conformations of the final product. The pathway to each product conformation has its own rate constant:

$$\dot{\alpha}_d = k_{d,f}(1 - \alpha) - k_{d,r}\alpha_d, \quad (2)$$

where the subscript d stands for either pathway 1 or pathway 2. The total activated population is the sum of the two conformations:

$$\alpha = \alpha_1 + \alpha_2. \quad (3)$$

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