UNDERSTANDING MECHANORESPONSIVE POLYMERS VIA MICROSTRUCTURALLY-BASED MODELS

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Summary Mechanically-induced reactivity is a promising means for designing self sensing and autonomous materials. Mechanically sensitive chemical groups called mechanophores can be covalently linked into polymers in order to trigger specific chemical reactions upon mechanical loading. Here, glassy PMMA and rubbery PMA each linked with mechanochromic molecules, are used as representative polymer architectures for building both understanding and quantitative models of mechanophore activation in bulk polymers.

INTRODUCTION

Mechanoresponsive polymers are created by covalently bonding force sensitive molecules, termed mechanophores, into bulk polymer architectures. Activation of the local chemical reaction (an electrocyclic ring opening converting spiropyran to its merocyanine form) is found to occur in response to macroscopic polymer deformation. The activation can be monitored via fluorescence associated with the merocyanine form of the mechanophore[1]. These mechanophores can therefore serve as probes into the local polymer environment and are ideal for determining design principles for smart materials based on alternative mechanophore chemistries. A microstructurally-based continuum model for the activation can help build quantitative understanding of the interaction between polymer architecture and molecular activation, and will set the groundwork for future mechanophore-based active material design.

EXPERIMENTS

In order to build both the probe and predictive capability, we investigate two mechanophore linked representative polymer architectures: elastomeric linear polymethacrylate (PMA) and glassy crosslinked polymethylmethacrylate (PMMA). For the linear system a mechanophore is at the center of each polymer chain. For the crosslinked system, the mechanophores constitute 2% of the crosslinks. Full field fluorescence is collected during mechanical testing in order to obtain simultaneous information on stress, strain, time, and mechanophore activation. Specifically, the crosslinked PMMA is characterized via solid cylinder torsion and the linear PMA is characterized via uniaxial tension. As expected, the two materials have fundamentally different mechanical responses (Figure 1a). PMMA is found to have an elastic-plastic mechanical behavior typical of glassy polymers with a linear elastic regime followed by a rate dependent yield peak which softens to a rate dependent minimum value and then exhibits moderate hardening. PMA is found to have a highly non-linear viscoelastic response typical of rubbery polymers. The two materials also have fundamentally different mechanophore activation responses (Figure 1a). The onset of mechanophore activation in PMMA is found to occur following post-yield softening at a shear strain and stress of roughly 0.3 and $30MPa$ respectively[3]. The activation then grows with strain with a gradually increasing slope. The onset of activation in PMA occurs at a significantly higher strain (~ 1.5) and significantly lower stress ($\sim 8MPa$). The activation then grows with an increasing slope that closely trails the shape of the stress-strain curve.

MODEL

A fully three dimensional continuum model is developed for the mechanical behavior and mechanophore activation in each polymer. These models take input from density functional theory (DFT) simulations of the spiropyran to merocyanine force-activated transformation, molecular dynamics simulations of the polymer architecture, polymer mechanics literature, and experimental data. The mechanical models are similar to those found in the literature and will not be discussed further here except to say they are sufficient to capture the rate dependent stress-strain response of each material over the range of conditions spanned experimentally.

The heart of the activation model is based on DFT simulations which reveal that the rate kinetics for conversion from the spiropyran to merocyanine form are strongly modified by the application of force across the mechanophore. In a bulk polymer, macroscopic stress provides the driving force for the spiropyran to merocyanine conversion. We therefore adopt a modified transition rate theory in which stress acts to reduce the spiropyran to merocyanine activation barrier with the form for the forward activation reaction given by equation 1:

$$\dot{\alpha} = \kappa \exp\left[-\frac{\Delta G}{R\theta}\left(1 - \frac{\sigma}{s_\alpha}\right)\right](1-\alpha) \tag{1}$$

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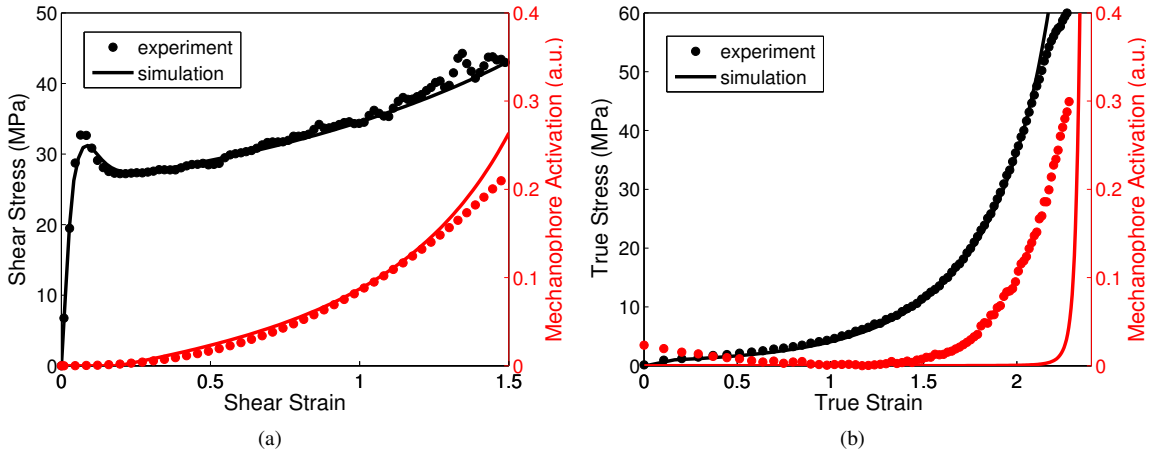

Figure 1. Mechanical and fluorescence activation response of two different mechanophore-linked polymer architectures: (a) response of crosslinked PMMA to shear loading, (b) response of linear PMA to tensile loading.

where α is the fraction of activated mechanophores, κ is an attempt frequency, ΔG is the activation barrier to the stress-free spiropyran to merocyanine transition, R is the universal gas constant, θ is absolute temperature, σ is an effective stress measure, and s_α has units of stress and acts to scale the transmitted force. The simplest approximation would be to assume that all of the macroscopic stress is always available to contribute to activating the mechanophores. This assumption is however clearly contradicted by the PMMA data (Figure 1a) in which activation only occurs after the yield peak. A constraint is therefore added to the activation equation which does not allow stress to be transmitted to the mechanophores until sufficient free volume evolution has occurred; free volume evolution has previously been closely tied with yield peak evolution[2, 4].

The activation model as given by equation 1 with the additional free volume constraint can be reasonably well fit to the monotonic PMMA data as shown in Figure 1a. In order to highlight the differences in the polymer architectures, the identical activation equations and parameters are then used to simulate mechanophore activation within PMA (Figure 1b). The model with these parameters predicts that the onset of activation occurs at a larger stress (and consequently strain) than seen experimentally. It also predicts that the material will reach full activation with minimal further increase in strain. This comparison highlights the difference in stress transmission in the two polymer architectures. Interestingly, this rather simple exercise does pick up on the qualitative result that activation will increase with strain more drastically in PMA than PMMA due to the strong nonlinearity in mechanical stress.

More sophisticated versions of the activation model are then developed for each polymer as motivated by the underlying architecture of each. The successes and failures of these models in capturing the activation within each polymer under monotonic, stress relaxation, and creep loading are used to deduce the governing physics. The quantitative implementation of each physical idea is found to greatly simplify the comparison among polymer architectures and loading histories, in particular allowing decomposition of the mechanophore rate dependence from the polymer rate dependence.

CONCLUSIONS

Representative mechanochromically linked rubbery and glassy materials were used as model systems for understanding mechanophore activation in solid state polymers. Microstructurally based continuum models were used to determine the pertinent physics and parameters for activation. These models are now ready to be adapted to examine force distribution in other polymers and to guide design of mechanophore based smart materials. **Acknowledgement.** This material is based upon work supported in part by the U. S. Army Research Laboratory and the U. S. Army Research Office under contract/grant number W911NF-07-1-0409 and in part by an Arnold and Mabel Beckman Foundation postdoctoral fellowship.

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