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ABSTRACT

Mechanically-induced reactivity is a promising means for designing self-reinforcing and self-healing materials. Mechanically sensitive chemical groups termed mechanophores can be covalently linked into polymers in order to trigger specific chemical reactions upon mechanical loading (Hickenboth et. al. 2007). Experimental groups are developing mechanophore-based schemes to trigger crosslinking within polymers when mechanical reinforcement is needed (Black et. al. 2011, Diesendruck et. al. 2013). Beyond the mechanophore chemistry many issues remain unsettled from a design perspective. What deformation history is required to trigger chemical response? Over what time scales will the reinforcing reaction occur? What do these time scales depend on? How much crosslinking produces a significant change in mechanical behavior? What is a desirable mechanical property change from a structural performance perspective? Theoretical and computational approaches can address some of these questions and accelerate design of self-reinforcing polymers. Previously we developed a microstructurally-based continuum model for the opto-mechanical response of a mechanophore-linked elastomer (Silberstein et. al, submitted). This model was specified to spiropyran-linked polymethacrylate, where spiropyran is a fluorescent mechanophore and polymethacrylate is a viscous elastomer. Comparison with corresponding uniaxial tensile experimental data showed that the model provides a reasonable lower bound to the material behavior. Here we extend this model to predict behavior for an elastomer with a chemically active mechanophore. The mechanical stress caused by macroscopic deformation is transferred by the polymer chain segments to force on the mechanophores. This force modifies the mechanophore energetics according to Bell theory promoting the mechanophore reaction (Bell 1978). The mechanophore reaction then catalyzes a crosslinking reaction, assigned as either instantaneous or time delayed. The crosslinking change in turn modifies both the local force distribution on the mechanophores and the macroscopic stress. Initial crosslinking density, mechanophore inclusion density, and mechanophore energetics are studied parametrically. Optimal conditions for demonstrating self-reinforcing elastomers are identified.