Large deformations and fluorescence response of mechanochromic polyurethane sensors

Filippo Cellini [a], Liwei Zhou [a], Sachin Khapli [b], Sean D. Peterson [a,c],
Maurizio Porfiri [a,*]

[a] Department of Mechanical and Aerospace Engineering, Tandon School of Engineering, New York University, Six MetroTech Center, Brooklyn, NY 11201, USA
[b] Engineering Division, New York University Abu Dhabi, Abu Dhabi 129188, United Arab Emirates
[c] Department of Mechanical and Mechatronics Engineering, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

ABSTRACT

A mechanochromic composite comprises an excimer-forming fluorescent dye dispersed in a compatible polymeric host. Upon large deformation of the polymeric structure, a shift of the fluorescence emission from the excimer band to the monomer band is observed, due to re-organization of dye aggregates. Mechanochromic elastomers can be tailored to produce a reversible optical response during cyclic deformation. Here, we study the optomechanical properties of mechanochromic elastomers undergoing large uniaxial and biaxial deformations. Through detailed experiments and constitutive modeling, we relate the optical response of the mechanochromic elastomer to the deformation of the polymer network. We confirm that optical response is largely reversible and is modulated by the initial dye concentration in the polymer. We adapt the classical Arruda–Boyce model to elucidate microstructural modifications of the polymer–dye blend. We propose a constitutive hypothesis for the optical behavior of the material, which relates variations of the emission spectrum to surface stretching. This knowledge can aid in the design of strain and stress sensors for applications in mechanics, biomechanics, and life sciences.

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1. Introduction

The increasing interest of the scientific community in active materials that are able to convert mechanical stimuli into electrical or optical signals is fueled by their incredible number of applications in mechanics, biomechanics, and the life sciences (Ferrari et al., 2007; Cohen Stuart et al., 2010; Urban, 2011; Venugopal et al., 2014; Cheng et al., 2012; Harrison and Ounaies, 2002; Jo et al., 2013). Synthetic polymers are attractive to these fields of investigation for the possibility of tailoring their properties through modification of their chemical and physical structures (Debashish et al., 2010; Weder, 2011).

Several efforts have been devoted to the study of polymeric materials whose optical properties are modulated in response to mechanical deformation (Roberts and Holder, 2011; Pucci and Ruggeri, 2011). For example, mechanochromism has been demonstrated in soft polymeric materials embedding excimer-forming fluorescent molecules, where shifts in relative intensity of monomer to excimer emission are observed upon deformation of the polymer host and reorganization of dye aggregates (Crenshaw et al., 2007; Donati et al., 2008; Kunzelman et al., 2006; Pucci et al., 2005; 2011). Mechanochemical polymers present a detectable modification of their optical behavior upon rupture of a covalent bond from the stretching of

* Corresponding author. Tel.: +16469973681; fax: +16469973532.
E-mail address: mporfiri@nyu.edu (M. Porfiri).

polymer chains (Davis et al., 2009; May and Moore, 2013). More specifically, the rupture of a weak covalent bond in a chromogenic molecule induces reversible (Sottos, 2014) or irreversible (Kingsbury et al., 2011) shifts in the fluorescence emission of the material. Beyond fluorescent materials, light emission has been detected in chemoluminescent materials upon activation of mechanochemical reactions (Chen et al., 2012; Chen and Sijbesma, 2014). Mechanochromic behavior has also been observed in soft photonic gels, where an applied stress induces a shift in the band gap of the photonic crystal, resulting in a variation of the spectrum of the reflected light (Foulger et al., 2001; Chan et al., 2013).

A fully reversible response is a highly desirable characteristic for mechanochromic systems, where we seek to obtain a complete recovery of the original optical properties as the deformation of the material is removed. Reversible optical response in a mechanochromic polymer has been obtained by blending crosslinked poly(cyclooctene) (PCO) with an oligo(p-phenylene vinylene) dye (Kunzelman et al., 2008), in which the shape memory behavior of the polymer has been leveraged to invert the process of dye reorganization in the polymeric matrix. Reversible mechanochromism has also been observed in polyurethane elastomers, either by substitution of oligo(p-phenylene vinylene) in the molecular structure (Crenshaw and Weder, 2006) or by dispersion of bis(benzoxazolyl)stilbene dye within the polymer network (Bao et al., 2013; Cellini et al., 2014). Reversible response to mechanical stress has been recently demonstrated for mechanochemical polymers by embedding a chromogenic spiropyran molecule in the cross-linked structure of a poly(dimethylsiloxane) polymer (Gossweiler et al., 2014). Moreover, successive mechanochemical activations of the chromogenic bond have been observed (Larsen and Boydston, 2014), and the effect of elastomer relaxation on mechanochemical response has been investigated (Beiermann et al., 2014).

Polyurethane elastomers are attractive for the design of polymer–dye blends with reversible optical response (Bao et al., 2013; Cellini et al., 2014). These materials can sustain large deformations with an almost complete recovery of the original shape (Wang and Pinnavaia, 1998), enabling the cancellation of optomechanical modifications (Gossweiler et al., 2014; Kunzelman et al., 2008). Polyurethane elastomers are two phase systems, with a hard phase composed of diisocyanates dispersed in a soft phase network of polyol chains (Desai et al., 2000; Petrovic and Ferguson, 1991; Petrovic et al., 1998). Similar to filled rubbers (Bergstrom and Boyce, 1999), foams (Gupta et al., 2013; Rizzi et al., 2000; Thiyagasundaram et al., 2010), and gels (Deng and Pence, 2010; Wallmersperger et al., 2013), the structural morphology of polyurethane elastomers evolves during mechanical loading (Qi and Boyce, 2005). Shear stresses induced by chain stretching and the evolution of the material morphology favor the reorganization of dye aggregates, which is responsible for variations in the optical response of the polymer. The latter constitutes a mechanism that has been previously associated with mechanochromic response in different polymer–dye blends (Crenshaw et al., 2007; Donati et al., 2008; Kunzelman et al., 2006; Pucci et al., 2005). Furthermore, polyurethane elastomers are biocompatible materials (Stokes et al., 1995; Feng and Ye, 2011),

affording potential applications in the environmental and life sciences.

In this study, we investigate reversible mechanochromic behavior of thermoplastic polyurethane elastomers blended with bis(benzoxazolyl)stilbene dyes (TPU–BBS). Material response for large deformations under uniaxial and biaxial extensions is studied to elucidate the relationship between optical response and stretching of the elastomeric network, microstructural evolution of the polymer, and dye concentration. Salient mechanical and optical properties of mechanochromic TPU–BBS elastomers are identified from uniaxial stress-relaxation experiments. Samples are subject to complete loading–unloading cycles, composed of successive steps where the film is slowly stretched and then relaxes toward the equilibrium. This allows for the separation of time-dependent viscoelastic effects from time-independent chain stretching in the constitutive response of the polymer (Cellini et al., 2014; Qi and Boyce, 2005). To assess mechanochromic behavior in a more complex loading condition, mechanical stretch and fluorescence emission are measured during biaxial extension experiments. More specifically, we study the inflation–deflation cycle of a membrane, which is executed in a continuous one-step process to avoid creep during constant pressurization of the membrane. Mechanical testing of membranes has been often used to study polymeric (Selvadurai and Shi, 2012) and biological materials (Gambarotta et al., 2005).

Experimental results are interpreted through a modified form of the Arruda–Boyce model (Arruda and Boyce, 1993), which accounts for the evolution of the microstructure during deformation (Qi and Boyce, 2004; 2005). To describe the optical response during deformation of the material, we propose a new constitutive hypothesis, which relates the fluorescence emission to the surface stretching of the elastomer. This constitutive relationship is calibrated on experimental data using a single parameter that depends on the initial concentration of the dye.

The paper is organized as follows. In Section 2, we present a description of the experimental apparatus for optomechanical testing, and we introduce the constitutive model used for the analysis. Experimental results are reported and discussed in Section 3, while conclusions are summarized in Section 4. Appendix A succinctly describes the model used to interpret the results of the inflation test.

2. Materials and methods

2.1. Fabrication of mechanochromic materials

Mechanochromic polymer–dye blends are thermoplastic polyurethane (TPU ESTANE-90AE purchased from Lubrizol) blended with 0.1, 0.5, and 1.5 wt% (weight percent) of bis(benzoxazolyl)stilbene (BBS) fluorescent dye (Sigma Aldrich). Polymeric films with uniform thicknesses in the range 0.2–0.3 mm are obtained via solution casting following a standard procedure for fabrication of mechanochromic composites (Ciardelli et al., 2013). The dye is dispersed in dimethylformamide (99.8% purity, Sigma-Aldrich) and sonicated for 10 min. Solvent-dye solutions are prepared with dye concentrations of 0.1, 0.5, and 1.5 wt%. The solvent-dye