

## EXPERIMENTAL METHODS FOR CHARACTERIZING MECHANOCHEMICALLY ACTIVE POLYMERS

Sharlotte L.B. Kramer<sup>1</sup>, Brett A. Beiermann<sup>2</sup>, Cassandra M. Kingsbury<sup>3</sup>, Preston A. May<sup>4</sup>, Jeffrey S. Moore<sup>5</sup>, Scott R. White<sup>6</sup> and Nancy R. Sottos<sup>7</sup>

University of Illinois at Urbana- Champaign, Beckman Institute for Advanced Science and Technology, 405 North Mathews Ave., Urbana, IL 61801 USA.

Email: <sup>1</sup>[sbkramer@illinois.edu](mailto:sbkramer@illinois.edu), <sup>2</sup>[bbeierm2@illinois.edu](mailto:bbeierm2@illinois.edu), <sup>3</sup>[ckingsbu@illinois.edu](mailto:ckingsbu@illinois.edu), <sup>4</sup>[may14@illinois.edu](mailto:may14@illinois.edu), <sup>5</sup>[jsmoore@illinois.edu](mailto:jsmoore@illinois.edu), <sup>6</sup>[swhite@illinois.edu](mailto:swhite@illinois.edu) and <sup>7</sup>[n-sottos@illinois.edu](mailto:n-sottos@illinois.edu)

**Keywords:** chain alignment, fluorescence imaging, photoelasticity, spiropyran, mechanochemically active polymer

### ABSTRACT

Mechanophores are force-sensitive molecules that exhibit a chemical response to mechanical force and can be incorporated into polymer chains. Application of force to these polymers in turn can activate the mechanophore, producing an advantageous chemical response. One goal for these mechanochemically active polymers (MAPs) is to restore mechanical properties after damage, but this requires further development of appropriate mechanophores and their incorporation into polymers. The prelude to these self-healing MAPs is characterization of the mechanisms for effective transfer of globally applied forces to mechanophores, providing design guidelines for new self-healing MAPs.

In this presentation, we describe three major components of experiments for characterizing bulk solid MAPs: mechanical loading, a quantitative measure of mechanophore activation, and a probe of polymer conformation. The focus of the presentation is an experiment for determining the role of polymer chain alignment with the applied force in mechanophore activation, but we briefly describe experimental designs for characterizing mechanophore alignment with the applied force during activation and mechanophore activation through shear loading. We are investigating linear and crosslinked polymers with the spiropyran (SP) mechanophore, which undergoes a force-induced ring-opening reaction accompanied by color change and fluorescence.

For the polymer chain alignment study, we combine uniaxial tensile testing, full-field fluorescence imaging, and full-field photoelasticity. Conventionally, photoelasticity provides a spatial map of the difference of principal stresses due to a temporary stress-induced birefringence in a deformed polymer. We are utilizing photoelasticity to measure the temporal change in optical birefringence during a mechanical test, given by a linear retardation called in the isochromatic phase,  $\delta$  [1]. The optical birefringence,  $\Delta n$ , can be related to the polymer chain alignment in a uniaxial loading test by Herman's Orientation function [2],  $f$ :

$$\delta = 2\pi h \Delta n / \lambda \quad (1)$$

$$\Delta n = f \Delta n_o \quad (2)$$

$$f = \langle 3 \cos^2(\theta) - 1 \rangle / 2 \quad (3)$$

where  $h$  is the polymer thickness,  $\lambda$  is the wavelength of light,  $\Delta n_o$  is the birefringence for fully aligned polymer chains, and  $\theta$  is the angle of polymer chains relative to the loading direction. We determine  $\delta$  in full field using four phase-stepped images in a similar manner to Hobbes *et al.* [3], except we split the light after the specimens using two 1-D diffraction gratings, one in the x-direction and one in the y-direction. We select the four equal intensity beams, which were each diffracted once in  $x$  and once in  $y$ , and then redirect the beams to the same CCD camera for simultaneous image capture, which is important for time-dependent materials.

Fluorescence imaging provides evidence from mechanochemical activation. Force-induced ring opening of the SP to its MC form leads to fluorescence at 590-750 nm with either UV or 500-560 nm excitation. A single wavelength 532-nm laser diode is expanded to 1.0-mm diameter beam, resulting in a fluorescence emission of 590-750 nm, with a peak at 655 nm. A dual-carriage tensile load frame for the uniaxial testing ensures that the center of the tensile dogbone specimens remains in same location as the laser beam during the entire test. Typical results for birefringence, normalized red intensity for fluorescence, stress, and stretch ratio for an active linear PMA-SP-PMA are given in Figure 1. At a stretch ratio 6.7 for this specimen, the slope of the birefringence curve is decreasing, with the birefringence approaching a plateau  $\Delta n_0$ , and the slope of the normalized red intensity of the fluorescence begins to increase, signaling the onset of mechanophore activation. These results indicate that chain alignment is required for MAP activation. The hybrid experimental approach, as demonstrated in this polymer chain study and in other hybrid experiments briefly discussed in this presentation, enables characterization of effective mechanical activation of MAPs.

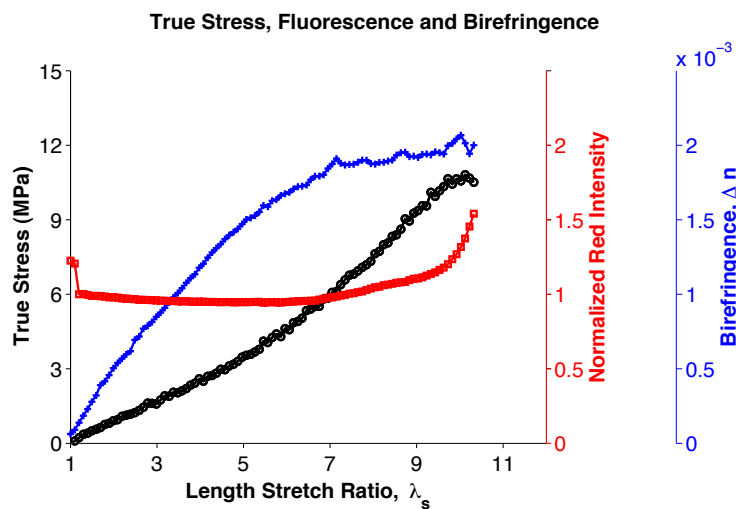


Figure 1: Typical true stress (black circles), fluorescence (red squares), and birefringence (blue crosses) vs. stretch ratio data for linear active SP-linked PMA under tensile loading. The slope of the curve of the red intensity, normalized by the initial intensity, begins to increase at a stretch ratio of 6.7, corresponding to the decrease in slope of the birefringence curve near a plateau.

The guiding principles behind these characterization experiments can inform future experimental design for self-healing MAPs. The degree of mechanophore activation will not necessarily correlate with effective healing, so experiments will need to decouple these variables and quantify both separately. Full-field optical methods can provide local data concerning spatial variations in activation, healing, and polymer conformation.

## REFERENCES

- [1] K. Ramesh, *Photoelasticity*, Springer Handbook of Experimental Solid Mechanics, Springer-Verlag Publishers, 2009, p. 701–742.
- [2] R. Wimberger-Friedl, The assessment of orientation, stress and density distributions in injection molded amorphous polymers by optical techniques, *Progress in Polymer Science*, **20**, 1995, p. 369–401.
- [3] J.W. Hobbs, R.J. Greene and E.A. Patterson, A novel instrument for transient photoelasticity, *Experimental Mechanics*, **43**, 2003, p. 403-409.