SHEAR ACTIVATION OF MECHANOPHORE-LINKED PMMA

Cassandra M. Kingsbury[1,4], Preston A. May[2,4], Scott R. White[3,4], Jeffrey S. Moore[2,1,4] and Nancy R. Sottos[1,4]

[1] Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign
1304 W. Green St., 61801, Urbana, Illinois, USA.
Email: ckingsbu@illinois.edu, n-sottos@illinois.edu

[2] Department of Chemistry, University of Illinois at Urbana-Champaign
505 S. Mathews Ave., 61801, Urbana, Illinois, USA.
Email: may14@illinois.edu, jsmoore@illinois.edu

[3]Department of Aerospace Engineering, University of Illinois at Urbana-Champaign
104 S. Wright St., 61801, Urbana, Illinois, USA.
Email: swhite@illinois.edu

[4]Beckman Institute for Advanced Science & Technology, University of Illinois at Urbana-Champaign
405 N. Mathews Ave., 61801, Urbana, Illinois, USA.

Keywords: Mechanochemistry, Torsion, Crosslinked, PMMA

ABSTRACT

A new strategy is employed to impart productive mechanochemical response to crosslinked polymers [1]. Force sensitive molecules, termed mechanophores, are successfully incorporated as co-crosslinkers into poly(methyl methacrylate) (PMMA) through a free radical polymerization initiated with benzoyl peroxide and N,N-dimethylaniline [2]. Evidence of a shear-activated local chemical reaction (an electrocyclic ring-opening) is provided by a color- and fluorescence-generating spiropyran mechanophore.

Crosslinked PMMA was synthesized with a total crosslink density of 1 mol%. For active or monofunctional control polymers, the spiropyran co-crosslinker content was held at 0.018 mol% with the remaining balance consisting of either ethylene glycol dimethacrylate (EGDMA), polyethylene glycol dimethacrylate with a molecular weight of 550 Da (PEG-550), or polyethylene glycol dimethacrylate with a molecular weight of 750 Da (PEG-750). Bulk polymerizations were performed in 1 mL syringes that had been compression molded into a tapered cylinder with a gauge length of 10 mm and a diameter of 2 mm.

Bulk polymer samples were studied under shear loading using a torsion test fixture and a TA Instruments AR-G2 rheometer [3]. Shear rates were held constant at 0.1 sec^{-1}, 0.01 sec^{-1}, and 0.001 sec^{-1} to allow the sample to undergo large strains in torsion and to produce color change and fluorescence in the active samples. Control samples were synthesized with either no spiropyran or a monofunctional spiropyran. These control samples showed no color change or change in fluorescence during shear rate testing. Visible color change in active PMMA-EGDMA samples as well as lack of color change in control PMMA-EGDMA samples is shown in Figure 1. Although not shown, PMMA-PEG550 and PMMA-PEG750 show similar results. In situ full field fluorescence imaging was used to determine a threshold stress and strain required for activation as a function of shear rate and polymer architecture, both of which have a significant effect on mechanochemical activity in the bulk polymer. As shown in Figure 2, increasing shear rate leads to an increase in activation stress, similar to bulk polymer yielding. Increasing the length of the primary crosslinker with respect to the spiropyran leads to a decrease in activation stress, while the activation strain (Table I) becomes more shear rate dependent with longer primary crosslinkers. Cross-sectional confocal fluorescence images correlated to the shear stress profile provided additional evidence that plastic flow is required for large scale

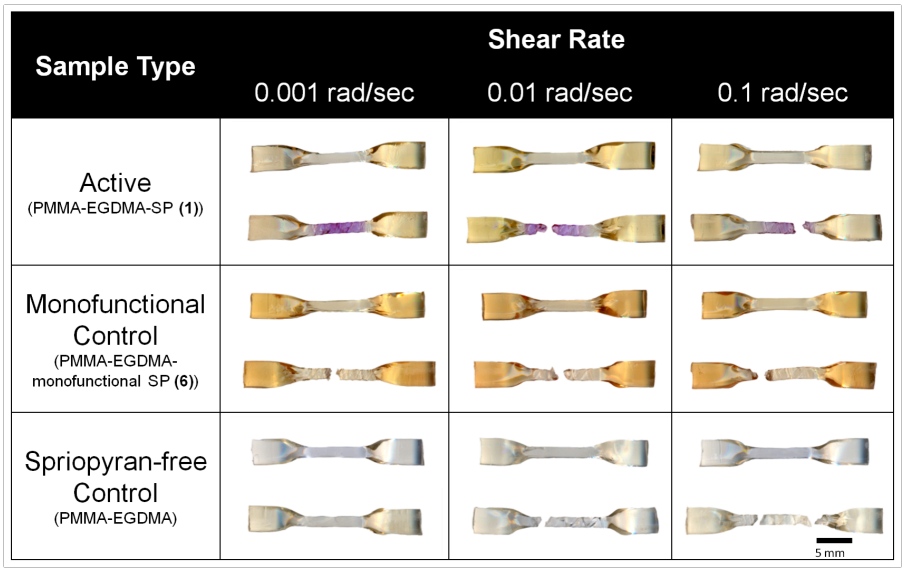

Fig. 1: Optical images of PMMA-EGDMA samples before (top) and after (bottom) torsional testing. Active samples display intense color change in the gauge section for all shear rates tested, while both control sample types do not.

activation. These findings show that the molecular details of the network architecture can be altered to tune the mechanochemical response. Torsional creep experiments are in progress to further probe the mechanisms of activation.

Table I: Activation strain for each polymer type and shear rate. Error is calculated as one standard deviation from the average.

Shear Rate	***PMMA-EGDMA***	***PMMA-PEG550***	***PMMA-PEG750***
0.001 rad/sec	45 ± 10 %	46 ± 5 %	45 ± 3 %
0.01 rad/sec	46 ± 6 %	45 ± 11 %	67 ± 7 %
0.1 rad/sec	48 ± 11 %	57 ± 15 %	77 ± 9 %

REFERENCES

[1] Potisek, S.L., Davis, D.A., Sottos, N.R., White, N.R., White, S.R., Moore, J.S., Mechanophore-Linked Addition Polymers, *J. Am. Chem. Soc.*, **129**, 2007, pp. 13808-13809.

[2] Davis, D.A., Hamilton, A., Yang, Y. Cremar, L.D., Gough, D.V., Potisek, S.L., Ong, M.T. Braun, P.V., Martínez, T.J., White, S.R., Moore, J.S., Sottos, N.R., Force-Induced Activation of Covalent Bonds in Mechanoresponsive Polymers, *Nature*, **459**, 2009, pp. 68-72.

[3] Kingsbury, C.M., May, P.A., Davis, D.A., White, S.R., Moore, J.S., Sottos, N.R., Shear Activation of Mechanophore-Crosslinked Polymers, *J. Mater. Chem.*, 2011, DOI: 10.1039/C0JM04015K

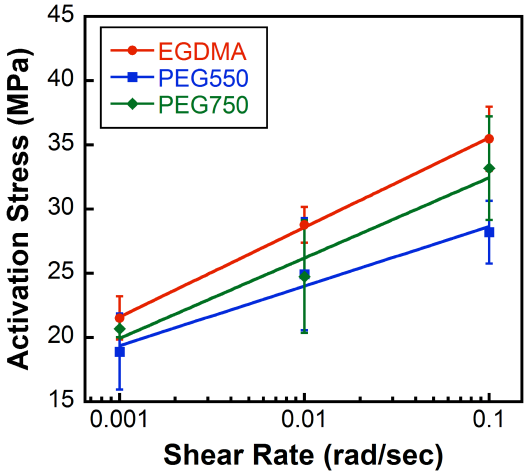

Fig. 2: Activation stress for each polymer type as a function of shear rate. Error bars reflect one standard deviation of the data.