ROUTING AND ACTION

MEMORANDUM

ROUTING

TO:(1) Sciences of Extreme Materials Branch (SEM) (Lambeth, Robert)

Report is available for review

(2) Proposal Files Report No.: Proposal Number: 66696-SM.15

DESCRIPTION OF MATERIAL

CONTRACT OR GRANT NUMBER: W911NF-15-1-0143

INSTITUTION: Duke University

PRINCIPAL INVESTIGATOR: Stephen L. Craig

TYPE REPORT: Final Report

DATE RECEIVED: 9/25/23 9:36AM

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TITLE: Final Report: Stress-strengthening Synthetic Polymers by Covalent Mechanochemistry

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ACTION TAKEN BY DIVISION

(x) Report has been reviewed for technical sufficiency and IS [x] IS NOT [ ] satisfactory.

( ) Based on my technical review, I have identified no OPSEC or Technology Protection concerns that need to be addressed regarding this report.

(x) Perfomance of the research effort was accomplished in a satisfactory manner and all other technical requirements have been fulfilled.

(x) Based upon my knowledge of the research project, I agree with the patent information disclosed.

Approved by robert.h.lambeth2.civ@mail.mil on 9/25/23 10:51AM

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13. SUPPLEMENTARY NOTES

The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT

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RPPR Final Report
as of 25-Sep-2023

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Proposal Number: 66696SM **Agreement Number: W911NF-15-1-0143**

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Begin Performance Period: 01-Jun-2015 **End Performance Period:** 31-May-2020
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Submitted By: Stephen L. Craig Email: stephen.craig@duke.edu
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Major Goals: Synthetic materials typically break down in response to the repeated cycles of mechanical load and stress that they experience during use. In polymer solutions, for example, shear-induced bond breaking reduces molecular weight and leads to a loss in viscosity, a problem that plagues oils and lubricants in high-performance engines. In solids, stress-induced bond scission or chain slippage can trigger micro-cracks that propagate and eventually lead to material failure. Many biological materials, however, remodel and become stronger in direct response to the mechanical forces that otherwise might cause them to fail. Bone and muscle, for example, build mass and strength when subjected to load, and wood and hair respond to force induced bond breaking at the molecular level by forming new bonds in the strained conformation, resulting in a net increase in strength. This project encompasses the design and synthesis of a family of synthetic polymers that channels the destructive energy responsible for bond scission into constructive, localized, bond-forming reactions that strengthen, rather than weaken, a polymeric material.

In this project, we are building off of our prior work, in which we demonstrated proof-of-concept for materials that grow 1-2 orders of magnitude stronger in response to typically destructive mechanical forces. These encouraging results inspire strategies for new stress-responsive materials and also raise previously unvoiced fundamental questions about the relationship between molecular level changes and bulk material properties. In particular, the current project addresses three specific research objectives:
(1) We are designing and synthesizing new, rapidly cross-linking mechanophores that report their state (unactivated, activated, cross-linked) through distinct spectroscopic signatures, and we will probe the interplay between molecular and macroscopic mechanical response in materials that incorporate them.
(2) We are designing and synthesizing new mechanophores that are both reversibly activated and reversibly cross-linkable, so that materials that incorporate them will become stiffer/stronger under load and softer/weaker in periods of rest.
(3) We are devising mechanophore based strategies in which mechanophore activation can be amplified (e.g., by initiating polymerization) to build mass and change properties in response to local mechanical signals within a material, and characterize the accompanying changes in material properties.

Accomplishments: 1. A new stress-strengthening system based on benzocyclobutene mechanophores. We developed synthetic methods that gave access to polymers containing multiple benzocyclobutene (BCB) mechanophores along the polymer backbone. When solutions of the BCB polymer were exposed to the normally destructive elongational flow forces generated by pulsed ultrasonication, the number of intermolecular bond-forming reactions was greater than the number of bond-breaking reactions, leading to a net increase in polymer molecular weight. The molecular weight increase could be turned into gelation by introducing a bismaleimide cross-linker that reacts with the ortho-quinodimethide intermediate generated by mechanically assisted ring opening of the BCB mechanophores and using polymer concentrations in excess of the critical overlap concentration. Unlike a previous mechanically induced gelation of a mechanophore-based polymer, the BCB cross-linking requires no ionic components and represents an attractive, second platform for stress-strengthening materials. The success of butadiene-type cycloaddition reactions in this context motivated the design of new, multi-responsive mechanophores described below.

2. Stress-initiated cross-linking via a new class of ferrocene mechanophores. Ferrocenophane mechanophores provide tunable activation, distinct and tunable spectroscopic shifts upon activation, and rapid cross-linking chemistry. Intrinsic force-free as well as force-coupled reactivity can be controlled through the size of an ansa bridge between cyclopentadiene ligands. In addition, changes in spectroscopic signatures can be programmed through the choice of free ligand to scavenge mechanically released Fe2+. Notably, this color change is irreversible under ambient conditions, and to the eye provides a colorimetric indication of strain that is comparable to that generated by other mechanochromic force probes such as spiropyran and napthpyran derivatives. It therefore provides a useful tool for permanent color change that can be used to report on past damage history in materials. Importantly, the cross-linking can occur even when released iron is scavenged, and so spectroscopy and cross-linking can be manipulated independently of each other.

A key aspect of the ferrocenophanes is that their mechanical susceptibility is among the greatest of the cross-linking mechanophores we have developed to date. This is despite the fact that ferrocene is classically regarded as being highly inert owing to the large dissociation energy of metal-cyclopentadienyl (Cp) bonds, but our quantitative studies reveal that the mechanical lability of the Fe-Cp bond is similar to that of the carbon-nitrogen bond of an azobisdialkylnitrile (bond dissociation energy < 30 kcal/mol), despite the significantly greater force-free stability of the Fe-Cp bond. This means that the ferrocenophanes offer a notable combination of being highly inert without force, but quite active as mechanophores.

3. Scalable mechanoacids. We found that alkoxy-substituted gem-dichlorocyclopropane mechanophores spontaneously eliminate HCl when activated, making them useful mechanoacids. The thermal stability of the mechanophores is quite substantial – the half-life for reaction is still on the order of hours even at 139 °C, and so these mechanophores possess a “goldilocks” character of force-free stability and force-coupled activity. A significant accomplishment was to show that this mechanophore can be activated in bulk elastomeric materials and combined with a pH indicator to give a colorimetric response.

4. Latent reactivity of epoxide mechanophores. Epoxides represent attractive modifications of unsaturated polymer backbones for mechanically coupled cross-linking, but they suffer from limited mechanical reactivity. We found that placing alkenes adjacent to cis-epoxide mechanophores along a polymer backbone results in ring-opening to carbonyl ylides during sonication, whereas epoxides with an adjacent saturated, linear alkyl chain do not. Upon release, tension-trapped ylides preferentially close to their trans-epoxides in accordance with the Woodward-Hoffman rules. The reactivity of carbonyl ylides is exploited to tag the activated species with spectroscopic labels and to facilitate force-induced cross-linking through a reaction with pendant alcohols on copolymers. The alkene effect is attributed to a combination of lower activation energy of the reaction ($\Delta G^\ddagger$) and greater force-coupled change in length as the reaction proceeds from the ground to transition state ($\Delta x^\ddagger$) relative to epoxides without the alkene. Even with alkene assistance, however, mechanochemical reactivity remains low; unlike the examples cited above, we have not been able to translate this reactivity from polymer solutions into bulk materials.

5. Methods and insights that quantitatively translate between molecular and bulk material behavior. This knowledge gap represents a key missing piece in the successful translation of covalent mechanochemistry into truly applied material systems. For example, we reported the quasi-static macroscopic response of silicone elastomers including cross-links made up of three spiropyran (SP) regioisomers. The relative colorimetric response of these regioisomers in the elastomers under quasi-static uniaxial tensile load matches their mechanical sensitivity. The extrapolated strain onset for detectable activation of all three regioisomers, however, is indistinguishable and occurs at ~90% uniaxial strain. The ratiometric response of the three isomers is constant across the strains investigated (90% - 135% uniaxial strain), in contrast to expectations based on simulations of strained intact polymer networks.

Work with our ARL collaborators on the same material systems, however, showed interesting differences in high strain processes relative to the quasi-static behavior described above. Interestingly, the onset strain at high strain rate is lower than that in the quasi-static testing, whereas the onset stress is actually higher. The mechanochromism therefore seems to be tied to relaxations that are too slow to be active at high strain rates. We extended this high strain rate work in a collaboration with Zhiyong Xia at the Applied Physics Lab (Johns Hopkins) to show that mechanochromic response can be used to see strain in high impact processes acting on soft materials in a way that is reminiscent of traumatic brain injury.

Finally, we quantified mechanically accelerated cis-to-trans isomerization of azobenzene in a silicone elastomer at lower strains (40-90%) than had been examined to date. The simple, single-exponential first-order kinetics in the unstrained PDMS became multi-exponential under strain. We found that very simple two-phase kinetic models can be used to characterize what must be much more complex kinetics in these systems. The kinetics are used to estimate the population of high force strands in the networks as a function of strain, and we found excellent agreement with estimates of average molecular force for the whole population based on simple models of affine deformation

6. Integration into soft devices. We collaborated with Prof. Hyunhyub Ko (UNIST, Korea) to demonstrate that a hierarchical composite architecture in porous mechanochromic composites can enhance both mechanochromic strain/stress sensitivity and stretchability. We evaluated structure–activity relationships both experimentally and through computational modelling, and the results of that work establish that reducing pore size while increasing the size of embedded silica nanoparticles at the pore surface enhance the mechanochromic sensitivity. Most material modifications that enhance the onset of mechanochromism also reduce extensibility, because polymer chains approach their maximum extension. The hierarchical architecture of the porous composite simultaneously reduces the onset strain and enhances extensibility.

Training Opportunities: Multiple students received training and mentoring in monomer design and synthesis, polymer synthesis, materials property characterization, theoretical polymer physics, image analysis, and experimental design related to the varied interdisciplinary aims of the project. In addition, graduate student trainees served as mentors for undergraduate students. Graduate students also had the opportunity to collaborate with researchers at a variety of institutions, including: UNIST (Korea), APL, the Army Research Lab, the University of South Carolina, and the Russian Academy of Sciences. In addition to technical and mentoring skills development, during the past project period students also were active in preparing and presenting public talks, writing papers, and project management -- including safety training and responsible conduct in research.
We participated in the Undergraduate Research Apprenticeship Program (Vivian Lu).

Results Dissemination: J. Wang, I. Piskun, and S. L. Craig, “Mechanochemical Strengthening of a Multi-mechanophore Benzocyclobutene Polymer,” ACS Macro Lett, 2015, 4, 834–837.

B. H. Bowser and S. L. Craig, “Empowering Mechanochemistry with Multi-mechanophore Polymer Architectures,” Polym. Chem., 2018, 9, 3583 - 3593. (partial)

Y. Sha, Y. Zhang, E. Xu, Z. Wang, T. Zhu, S. L. Craig, and C. Tang, “Quantitative and Mechanistic Mechanochemistry in Ferrocene Dissociation,” ACS Macro Lett., 2018, 7, 1174-1179.

Y. Lin, M. H. Barbee, C. C. Chang, and S. L. Craig, “Regiochemical Effects on Mechanophore Activation in Bulk Materials,” J. Am. Chem. Soc., 2018, 140, 15969-15975.

Z. Xia, V. D. Alphonse, D. B. Trigg, T. P. Harrigan, J. M. Paulson, Q. T. Luong, E. P. Lloyd, M. H. Barbee, and S. L. Craig, “‘Seeing’ Strain in Soft Materials,” Molecules 2019, 24, 542.

J. Park, Y. Lee, M. H. Barbee, S. Cho, S. Cho, R. Shanker, J. Kim, J. Myoung, M. P. Kim, C. Baig, S. L. Craig, and H. Ko, “Hierarchical Nanoparticle-in-Micropore Architecture for Enhanced Mechanosensitivity and Stretchability in Mechanochromic Electronic Skins,” Adv. Materials, 2019, 31, 1808148.

Y. Lin, H. R. Hensen, W. J. Brittain, and S. L. Craig, “Strain-dependent Kinetics in the cis-to-trans Isomerization of Azobenzene in Bulk Elastomers,” J. Phys. Chem. B., 2019, 40, 8492-8498.

Y. Sha, Y. Zhang, T. Zhu, S. Tan, S. L. Craig, C. Tang, “Generalizing Metallocene Mechanochemistry to Ruthenocene Mechanophores,” Chem. Sci., 2019, 10, 4959-4965.

M. H. Barbee, J. Wang, T. B. Kouznetsova, M. Lu, and S. L. Craig, “Mechanochemical Ring-opening of Allylic Epoxides,” Macromolecules, 2019, 16, 6234-6240.

Y. Lin, T. B. Kouznetsova, and S. L. Craig, “A Latent Mechanoacid for Time-Stamped Mechanochromism and Chemical Signaling in Polymeric Materials,” J. Am. Chem. Soc., 2020, 142, 99-103.

Y. Zhang, Z. Wang, T. B. Kouznetsova, Y. Sha, E. Xu, L. S. Shannahan, M. Fermen-Coker, Y. Lin, C. Tang, and S. L. Craig, “Distal Conformational Locks on Ferrocene Mechanophores Guide Reaction Pathways for Increased Mechanochemical Reactivity,” Nature Chem., 2021, 13, 56-62. (partial)

L. S. Shannahan, Y. Lin, J. F. Berry, M. H. Barbee, M. Fermen-Coker, and S. L. Craig, “Onset of Mechanochromic Response in the High Strain Rate Uniaxial Compression of Spiropyran Embedded Silicone Elastomers,” Macromol. Rapid Commun., 2021, 42, 202000449. DOI: 10.1002/marc.202000449.

Over the project period, the results were presented in 51 invited talks by the PI at academic institutions, corporations, and professional meetings in the U.S. and internationally during the reporting period. Students and postdocs from the group have presented at least 20 additional contributed talks across the project period.

Honors and Awards: G. Stafford Whitby Memorial Lectureship, University of Akron (2017)
Duke Senior Honor Award (2016, 2017)
Arun Guthikonda Memorial Award and Lecture, Columbia University (2015)

Protocol Activity Status:

Technology Transfer: Our work involved collaboration with Fermen-Coker and team at ARL, and teleconferences with Shaun Filocamo, Chris Doona, and June Lum at Natick. We also collaborated with staff at the Applied Physics Lab at JHU who have long research relationships with ARO/ARL.

PARTICIPANTS:

Participant Type: PD/PI
Participant: Stephen Craig
Person Months Worked: 4.00 **Funding Support:**

Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Brandon Bowser
Person Months Worked: 5.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Patricia Johnson
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Cameron Brown
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Meredith Barbee
Person Months Worked: 4.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Junpeng Wang
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Yangju Lin
Person Months Worked: 11.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Yudi Zhang
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Chia-Chih Chang
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Anthony DiLauro
Person Months Worked: 4.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Undergraduate Student
Participant: Meilin Lu
Person Months Worked: 3.00 **Funding Support:**
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Participant Type: Undergraduate Student
Participant: Ethen Lund
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ARTICLES:

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Article Title: Mechanochemical Strengthening of a Multi-mechanophore Benzocyclobutene Polymer
Authors: Junpeng Wang, Ilya Piskun, Stephen L. Craig
Keywords: polymers, mechanochemistry, stress-responsive, cross-linking
Abstract: The mechanical stresses that materials experience during use can lead to aging and failure. Recent developments in covalent mechanochemistry have provided a mechanism by which those stresses can be channeled into constructive, rather than destructive, responses, including strengthening in materials. Here, the synthesis and mechanical response of a polymer containing multiple benzocyclobutene (BCB) mechanophores along its backbone are reported. When solutions of the BCB polymer were exposed to the normally destructive elongational flow forces generated by pulsed ultrasonication, the number of intermolecular bond-forming reactions was greater than the number of bond-breaking reactions, leading to a net increase in polymer molecular weight. The molecular weight increase could be turned into gelation by introducing a bismaleimide cross-linker that reacts with the ortho-quinodimethide intermediate generated by mechanically assisted ring opening of the BCB mechanophores and using polymer con
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Date Submitted: 8/31/18 12:00AM Date Published:
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Article Title: Empowering mechanochemistry with multi-mechanophore polymer architectures
Authors: Brandon H. Bowser, Stephen L. Craig
Keywords: mechanochemistry, mechanophores, polymer synthesis
Abstract: The development of multi-mechanophore polymers (MMPs) has empowered new methodologies for observing, quantifying, and exploiting mechanochemical transformations. For example, techniques such as single molecule force spectroscopy and pulsed ultrasound can be used to induce and observe up to hundreds of chemical reactions within a single polymer, enabling mechanistic insights into mechanochemical reactivity. At the same time, MMPs allow for the substantial mechanochemical remodeling of polymers and associated change in material properties. This minireview presents synthetic approaches that have been used to make MMPs, methods that have been developed to probe and characterize their reactivity, and changes in properties that have been observed through their mechanochemical response.
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Volume: 24 Issue: 3 First Page #: 542
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Article Title: 'Seeing' Strain in Soft Materials
Authors: Zhiyong Xia, Vanessa D. Alphonse, Doug B. Trigg, Tim P. Harrigan, Jeff M. Paulson, Quang T. Luong,
Keywords: Mechanochemistry, traumatic brain injury, ballistics
Abstract: Several technologies can be used for measuring strains of soft materials under high rate impact conditions. These technologies include high speed tensile test, split Hopkinson pressure bar test, digital image correlation and high speed X-ray imaging. However, none of these existing technologies can produce a continuous 3D spatial strain distribution in the test specimen. Here we report a novel passive strain sensor based on poly(dimethyl siloxane) (PDMS) elastomer with covalently incorporated spiropyran (SP) mechanophore to measure impact induced strains. We have shown that the incorporation of SP into PDMS at 0.25 wt% level can adequately measure impact strains via color change under a high strain rate of 1500 s?1 within a fraction of a millisecond. Further, the color change is fully reversible and thus can be used repeatedly. This technology has a high potential to be used for quantifying brain strain for traumatic brain injury applications.
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Article Title: Hierarchical nanoparticle-in-micropore architecture for enhanced mechanosensitivity and stretchability in mechanochromic electronic skins
Authors: J. Park, Y. Lee, M. H. Barbee, S. Cho, S. Cho, R. Shanker, J. Kim, J. Myoung, M. P. Kim, C. Baig, S. L.
Keywords: mechanochromism, electronic skin, composites
Abstract: Biological tissues are multi-responsive and functional, and similar properties might be possible in synthetic systems by merging responsive polymers with hierarchical soft architectures. For example, mechanochromic polymers have applications in force- responsive colourimetric sensors and soft robotics, but their integration into sensitive, multi-functional devices remains challenging. Herein, we report a hierarchical nanoparticle-in-micropore (NP-MP) architecture in porous mechanochromic polymers to enhance the mechanosensitivity and stretchability of mechanochromic electronic skins (e-skins). The hierarchical NP-MP structure results in stress concentration- induced mechanochemical activation of mechanophores, significantly improving the mechanochromic sensitivity to both tensile strain and normal force (critical tensile strain: 50% and normal force: 1 N). Furthermore, the porous mechanochromic composites exhibit a reversible mechanochromism under a strain of 250%. This architecture
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Date Submitted: 8/13/19 12:00AM Date Published: 11/7/18 5:00AM
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Article Title: Ring-Closing Metathesis and Ring-Opening Metathesis Polymerization toward Main-Chain Ferrocene-Containing Polymers
Authors: Ye Sha, Yudi Zhang, Tianyu Zhu, Shaobo Tan, Yujin Cha, Stephen L. Craig, Chuanbing Tang
Keywords: ferrocene, ring opening metathesis, crystallization, assembly
Abstract: We report the preparation of cyclic ferrocenyl olefins with various substituents and different ring sizes by ring-closing metathesis (RCM). These ferrocene-containing monomers were subject to ring-opening metathesis polymerization (ROMP), leading to main-chain ferrocene-containing homopolymers, random copolymers, and block copolymers. Depending on the substituents, ferrocenyl homopolymers are semicrystalline or amorphous with good solubility. A semicrystalline polymer was used in the crystallization-driven self-assembly (CDSA) of block copolymers to generate platelet nanostructures.
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Article Title: Regiochemical Effects on Mechanophore Activation in Bulk Materials
Authors: Yangju Lin, Meredith H. Barbee, Chia-Chih Chang, Stephen L. Craig
Keywords: mechanochemistry, regiochemistry
Abstract: Mechanochromic force probes, including spiropyran derivatives, have proven to be useful in visualizing the stress/strain distribution and fracture behavior in polymeric materials. Here, we report the macroscopic response of silicone elastomers including cross-links made up of three spiropyran (SP) regioisomers. The SP derivatives SP(o), SP(m), and SP(p) are connected to the network through an identical attachment point on the indoline fragment and regioisomeric attachments ortho, meta, and para to the spirocyclic C–O bond on the benzaldehyde fragment, respectively. The relative colorimetric response of these regioisomers under quasi-static uniaxial tensile load is SP(o) > SP(m) > SP(p), consistent with the expected mechanical sensitivity of the regioisomers obtained from molecular modeling. The extrapolated strain onset for detectable activation of all three regioisomers, however, is indistinguishable and occurs at ?90% uniaxial strain. Finally, the ratiometric response of the three...
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Article Title: Generalizing metallocene mechanochemistry to ruthenocene mechanophores
Authors: Ye Sha, Yudi Zhang, Enhua Xu, C. Wayne McAlister, Tianyu Zhu, Stephen L. Craig, Chuanbing Tang
Keywords: ruthenocene, mechanochemistry

Abstract: Recent reports have shown that ferrocene displays an unexpected combination of force-free stability and mechanochemical activity, as it acts as the preferred site of chain scission along the backbone of highly extended polymer chains. This observation raises the tantalizing question as to whether similar mechanochemical activity might be present in other metallocenes, and, if so, what features of metallocenes dictate their relative ability to act as mechanophores. In this work, we elucidate polymerization methodologies towards main-chain ruthenocene-based polymers and explore the mechanochemistry of ruthenocene. We find that ruthenocene, in analogy to ferrocene, acts as a highly selective site of main chain scission despite the fact that it is even more inert. A comparison of ruthenocene and ferrocene reactivity provides insights as to the possible origins of metallocene mechanochemistry, including the relative importance of structural and thermodynamic parameters such as...

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Article Title: Mechanochemical Ring-Opening of Allylic Epoxides
Authors: Meredith H. Barbee, Junpeng Wang, Tatiana Kouznetsova, Meilin Lu, Stephen L. Craig
Keywords: polymer mechanochemistry, epoxides, sonication, cross-linking

Abstract: Recent successes in covalent polymer mechanochemistry might more easily be translated to stress-responsive bulk materials if easily scalable and minimalist mechanophores were identified. Epoxides represent attractive modifications of unsaturated polymer backbones for this purpose, but they suffer from limited mechanical reactivity. Here, we report that placing alkenes adjacent to cis-epoxide mechanophores along a polymer backbone results in ring-opening to carbonyl ylides during sonication, whereas epoxides with an adjacent saturated, linear alkyl chain do not. Upon release, tension-trapped ylides preferentially close to their trans-epoxides in accordance with the Woodward?Hoffmann rules. The reactivity of carbonyl ylides is exploited to tag the activated species with spectroscopic labels and to facilitate force-induced cross-linking through a reaction with pendant alcohols on co-polymers. The alkene effect is attributed to a combination of lower activation energy of the reaction...

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Article Title: A Mechanochemistry-Based Technique For Early Material Damage Detection In High Strain Rate Processes
Authors: Logan Shannahan, James Berry, Yangju Lin, Meredith Barbee, Stephen Craig, Daniel Casem, Muge Fe
Keywords: science, synthetic polymers, elastomers, molecules, polymers, fungi, alkenes, chemical synthesis, mechanochemistry
Abstract: It is often desired to detect damage at the sub-continuum level before continuum-level damage is observed. The burgeoning field of polymer mechanochemistry promises development of novel materials that would report sub-continuum-level damage if a critical stress or strain level is exceeded. In addition, a long-standing challenge for multi-scale modeling validation has been the generation of experimental data to link molecular-level damage to macroscopic material behavior at high rate. Using mechanophore-embedded silicone elastomer samples, for the first time ever, molecular-level bond breakage is captured visually during standard high-rate material characterization experiments, prior to the onset of macroscopic damage. A brief description of synthesized mechanophores, methods of embedding into the silicone elastomer, and the method to determine the critical strain of mechanophore activation (molecular-level bond breakage) is included. The critical strain and critical stress values...
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Article Title: A Latent Mechanoacid for Time-Stamped Mechanochromism and Chemical Signaling in Polymeric Materials
Authors: Yangju Lin, Tatiana B. Kouznetsova, Stephen L. Craig
Keywords: Network chemistry
Abstract: Mechanically coupled proton transduction offers potential for stress-responsive polymeric materials whose properties can be switched via acid-triggered coloration, polymerization/cross-linking, or degradation. The utility of currently available mechanoacids, however, is limited by modest force-free stability or a scissile response that caps mechanoacid generation at one proton per strained polymer chain. Here, we report a new mechanoacid based on 2-methoxy-substituted gem-dichlorocyclopropane (MeO-gDCC). Pulsed ultrasonication leads to the mechanochemical ring opening of the MeO-gDCC and the subsequent elimination of either HCl or MeCl, with ? 0.58 equiv of HCl released per mechanophore activation and ?67 protons per chain scission event. Single-molecule force spectroscopy reveals that the methoxy substituent lowers the force required for rapid (kopen ?102 s–1) ring opening to ca. 900 pN, vs 1300 pN required for the parent gDCC. The utility of the mechanoacid is demonstrated in silicone
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Article Title: Distal conformational locks on ferrocene mechanophores guide reaction pathways for increased mechanochemical reactivity
Authors: Yudi Zhang, Zi Wang, Tatiana B. Kouznetsova, Ye Sha, Enhua Xu, Logan Shannahan, Muge Fermen-C
Keywords: Network chemistry
Abstract: Mechanophores can be used to produce strain-dependent covalent chemical responses in polymeric materials, including stress strengthening, stress sensing and network remodelling. In general, it is desirable for mechanophores to be inert in the absence of force but highly reactive under applied tension. Metallocenes possess potentially useful combinations of force-free stability and force-coupled reactivity, but the mechanistic basis of this reactivity remains largely unexplored. Here, we have used single-molecule force spectroscopy to show that the mechanical reactivities of a series of ferrocenophanes are not correlated with ring strain in the reactants, but with the extent of rotational alignment of their two cyclopentadienyl ligands. Distal attachments can be used to restrict the mechanism of ferrocene dissociation to proceed through ligand 'peeling', as opposed to the more conventional 'shearing' mechanism of the parent ferrocene, leading the dissociation rate constant to increase b
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Article Title: Onset of Mechanochromic Response in the High Strain Rate Uniaxial Compression of Spiropyran Embedded Silicone Elastomers
Authors: Logan S. Shannahan, Yangju Lin, James F. Berry, Meredith H. Barbee, Müge Fermen?Coker, Stephen
Keywords: Network chemistry
Abstract: The molecular processes that accompany dynamic mechanical response to large deformations at high strain rate (?1000 s?1 or higher) underlie the early stages of damage in materials, but understanding of material response in this regime is typically limited to macroscopic constitutive equations. Here, spiropyran mechanophores are embedded in very short, stress-bearing strands in silicone elastomers, and their mechanochromic response to uniaxial compression is explored in a Split Hopkinson Pressure (or Kolsky) Bar. At strain rates of 1000 s?1, the onset of mechanochromism occurs at lower strains, but higher stresses, than in the same materials under quasi-static loading. Similar to quasi-static loading, however, a negligible effect of mechanophore structure on the critical strain for colorimetric onset is observed. The results suggest that nonequilibrium, inhomogeneous local tension distributions in the elastomers lead to greater stress in individual strands than at the same strains under
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Article Title: Strain-Dependent Kinetics in the Cis-to-Trans Isomerization of Azobenzene in Bulk Elastomers
Authors: Yangju Lin, Heather R. Hansen, William J. Brittain, Stephen L. Craig
Keywords: Network chemistry

Abstract: The cis-to-trans isomerization of azobenzene is accelerated in a bulk PDMS elastomer under uniaxial tension. The kinetics are cleanly described by a single-exponential first-order process (k = 2.7 × 10–5 s–1) in the absence of tension but become multiexponential under constant strains of 40–90%. The complex kinetics can be reasonably modeled as a two-component process. The complex kinetics can be reasonably modeled as a two-component process.

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Partners

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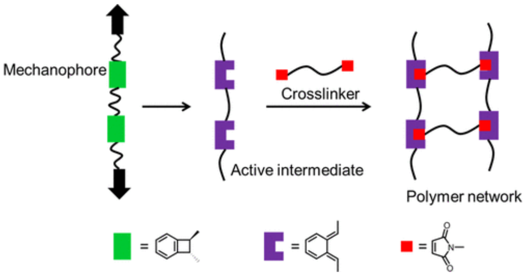
I certify that the information in the report is complete and accurate:
Signature: Stephen Craig
Signature Date: 9/25/23 9:36AM

Accomplishments

Major accomplishments from this project include:

In Year 1, we emphasize the development of new mechanophore cross-linking agents:

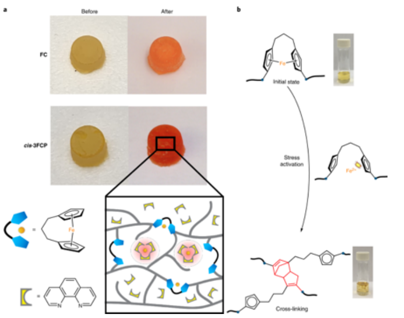
1. A new stress-strengthening system based on benzocyclobutene mechanophores. We developed synthetic methods that gave access to polymers containing multiple benzocyclobutene (BCB) mechanophores along the polymer backbone. When solutions of the BCB polymer were exposed to the normally destructive elongational flow forces generated by pulsed ultrasonication, the number of intermolecular bond-forming reactions was greater than the number of bond-breaking reactions, leading to a net increase in polymer molecular weight. The molecular weight increase could be turned into gelation by introducing a bismaleimide cross-linker that reacts with the *ortho*-quinodimethide intermediate generated by mechanically assisted ring opening of the BCB mechanophores and using polymer concentrations in excess of the critical overlap concentration. Unlike a previous mechanically induced gelation of a mechanophore-based polymer, the BCB cross-linking requires no ionic components and represents an attractive, second platform for stress-strengthening materials. The success of butadiene-type cycloaddition reactions in this context motivated the design of new, multi-responsive mechanophores described below.



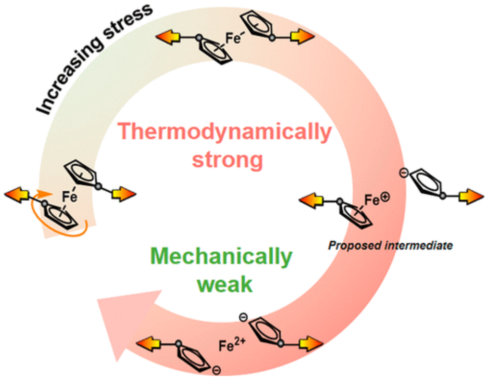
For reversible, multi-state systems, we also successfully synthesized a parent oxa-bicyclopentane (OBP) framework, complete with aryl bromides that could (we believed) be coupled to a range of functionality and used as a multi-state, stress-reporting and cross-linkable mechanophore. All indications were that our design was well chosen, except that the OBP scaffold was not as robust as envisioned. For example, we found that the presence of even small amounts of mild Lewis acids were sufficient to trigger an undesirable isomerization in concert with the desired coupling reaction. We began to deemphasize the reversible project.

In Year 2, further developed new cross-linking mechanophores in work that continued through Year 3 and our NCE Year 4, including:

2. Stress-initiated cross-linking via a new class of ferrocene mechanophores. Ferrocenophane mechanophores provide tunable activation, distinct and tunable spectroscopic shifts upon activation, and rapid cross-linking chemistry. Intrinsic force-free as well as force-coupled reactivity can be controlled through the size of an *ansa* bridge between cyclopentadiene ligands. In addition, changes in spectroscopic signatures can be programmed through the choice of free ligand to scavenge mechanically released Fe^{2+}. Notably, this color change is irreversible under ambient conditions, and to the eye provides a colorimetric indication of strain that is comparable to that generated by other mechanochromic force probes such as spiropyran and napthpyran derivatives. It therefore provides a useful tool for permanent color change that can be used to report on past damage history in materials. Importantly, the cross-linking can occur even when released iron is scavenged, and so spectroscopy and cross-linking can be manipulated independently of each other.

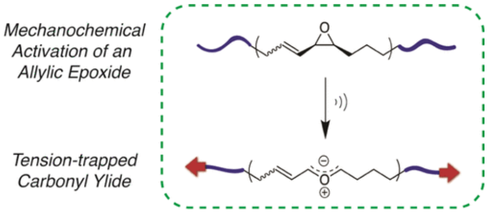


A key aspect of the ferrocenophanes is that their mechanical susceptibility is among the greatest of the cross-linking mechanophores we have developed to date. This is despite the fact that ferrocene is classically regarded as being highly inert owing to the large dissociation energy of metal-cyclopentadienyl (Cp) bonds, but our quantitative studies reveal that the mechanical lability of the Fe-Cp bond is similar to that of the carbon-nitrogen bond of an azobisdialkylnitrile (bond dissociation energy < 30 kcal/mol), despite the significantly greater force-free stability of the Fe-Cp bond. This means that the ferrocenophanes offer a notable combination of being highly inert without force, but quite active as mechanophores.



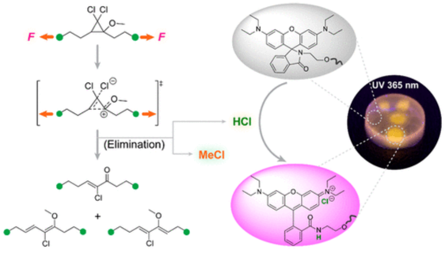
In Years 3 and 4, we completed work on metastable, reactive states of additional mechanophores, discovered the release of acid that could potentially be used to trigger cross-linking through catalysis, and transitioned into studies that probe how sensitive mechanochemistry is to various mechanical contexts.

3. Latent reactivity of epoxide mechanophores. Epoxides represent attractive modifications of unsaturated polymer backbones for mechanically coupled cross-linking, but they suffer from limited mechanical reactivity. We found that placing alkenes adjacent to *cis*-epoxide mechanophores along a polymer backbone results in ring-opening to carbonyl ylides during sonication, whereas epoxides with an adjacent saturated, linear alkyl chain do not. Upon release, tension-trapped ylides preferentially close to their *trans*-epoxides in accordance with the Woodward-Hoffman rules. The reactivity of carbonyl ylides is exploited to tag the activated species with spectroscopic labels and to facilitate force-induced cross-linking through a reaction with pendant alcohols on copolymers. The alkene effect is attributed to a

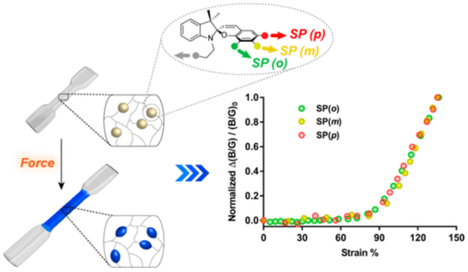


combination of lower activation energy of the reaction ($\Delta G^{\ddagger}$) and greater force-coupled change in length as the reaction proceeds from the ground to transition state ($\Delta x^{\ddagger}$) relative to epoxides without the alkene. Even with alkene assistance, however, mechanochemical reactivity remains low; unlike the examples cited above, we have not been able to translate this reactivity from polymer solutions into bulk materials.

4. Scalable mechanoacids. We found that alkoxy-substituted *gem*-dichlorocyclopropane mechanophores spontaneously eliminate HCl when activated, making them useful mechanoacids. The thermal stability of the mechanophores is quite substantial – the half-life for reaction is still on the order of hours even at 139 °C, and so these mechanophores possess a "goldilocks" character of force-free stability and force-coupled activity. A significant accomplishment was to show that this mechanophore can be activated in bulk elastomeric materials and combined with a pH indicator to give a colorimetric response.



5. Methods and insights that quantitatively translate between molecular and bulk material behavior. This knowledge gap represents a key missing piece in the successful translation of covalent mechanochemistry into truly applied material systems. For example, we reported the quasi-static macroscopic response of silicone elastomers including cross-links made up of three spiropyran (SP) regioisomers. The relative colorimetric response of these regioisomers in the elastomers under quasi-static uniaxial tensile load matches their mechanical sensitivity. The extrapolated strain onset for detectable activation of all three regioisomers, however, is indistinguishable and occurs at ~90% uniaxial strain. The ratiometric response of the three isomers is constant across the strains investigated (90% - 135% uniaxial strain), in contrast to expectations based on simulations of strained intact polymer networks.



Work with our ARL collaborators on the same material systems, however, showed interesting differences in high strain processes relative to the quasi-static behavior described above. Interestingly, the onset strain at high strain rate is lower than that in the quasi-static testing, whereas the onset stress is actually higher. The mechanochromism therefore seems to be tied to relaxations that are too slow to be active at high strain rates. We extended this high strain rate work in a collaboration with Zhiyong Xia at the Applied Physics Lab (Johns Hopkins) to show that mechanochromic response can be used to see strain in high impact processes acting on soft materials in a way that is reminiscent of traumatic brain injury.

Finally, we quantified mechanically accelerated *cis*-to-*trans* isomerization of azobenzene in a silicone elastomer at lower strains (40-90%) than had been examined to date. The simple, single-exponential first-order kinetics in the unstrained PDMS became multi-exponential under strain. We found that very simple two-phase kinetic models can be used to characterize what must be much more complex kinetics in these systems. The kinetics are used to estimate the population of high force strands in the networks as a function of strain, and we found excellent agreement with estimates of average molecular force for the whole population based on simple models of affine deformation

6. Integration into soft devices. We collaborated with Prof. Hyunhyub Ko (UNIST, Korea) to demonstrate that a hierarchical composite architecture in porous mechanochromic composites can enhance both mechanochromic strain/stress sensitivity and stretchability. We evaluated structure–activity relationships both experimentally and through computational modelling, and the results of that work establish that reducing pore size while increasing the size of embedded silica nanoparticles at the pore surface enhance the mechanochromic sensitivity. Most material modifications that enhance the onset of mechanochromism also reduce extensibility, because polymer chains approach their maximum extension. The hierarchical architecture of the porous composite simultaneously reduces the onset strain and enhances extensibility. An electronic skin based on the composite material was used in a wearable motion sensor and dual-mode touch audio sensor, enabling detection of static/dynamic force without any external power source.