Angewandte Highlights

Mechanochemistry

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Squeezing New Life Out of Polymers**

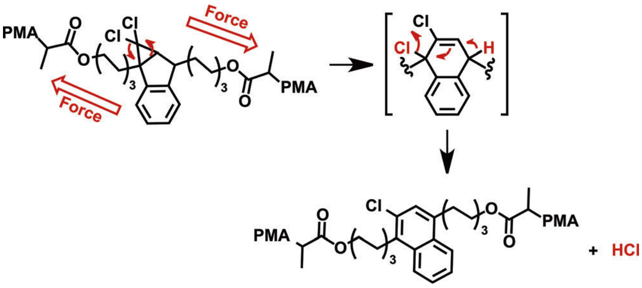
*Johnathan N. Brantley, Kelly M. Wiggins, and Christopher W. Bielawski**

catalysts · mechanochemistry · polymers · self-healing materials · sensors

The field of polymer mechanochemistry,[1,2] wherein macroscopic forces are translated into chemical transformations within polymeric matrices, is witnessing a rebirth. Unique or otherwise kinetically inaccessible chemical reactions are now possible when mechanically labile functionalities, termed mechanophores,[1] are embedded within polymers and then subjected to exogenous mechanical forces.[3–5] Paradigms in the field are shifting, however, and efforts are now focusing on using force as a method for driving the production of reactive chemical species. In particular, polymers that generate acids or redox reagents under the action of mechanical force are of interest, as such materials could find utility in applications that range from self-healing systems that undergo spontaneous repair through acid-catalyzed cross-linking reactions to mechanically driven syntheses.

The production of valuable small molecules from mechanically activated polymers is still in its infancy, and reported methods for achieving this goal often require a thermal or chemical treatment step.[6,7] Designing materials that extrude well-defined chemical entities solely under mechanical force has proven considerably more challenging. In a seminal contribution,[8] Moore and co-workers showed that dinitrogen could be expelled from a centrally positioned diazo unit in a poly(ethylene glycol) chain under ultrasonication. Although the chemical inertness of dinitrogen precluded its use in further reactions, this example laid the groundwork for two recent reports from the Moore and Grzybowski laboratories that beautifully demonstrated how reactive chemical reagents can be generated from mechanically responsive materials.

The Moore group focused on generating Brønsted acids by compressing appropriately functionalized polymers.[9] The design of the mechanically responsive materials was based on previous studies from Craig et al., who demonstrated that polymers containing multiple *gem*-dihalocyclopropane (*g*DHC) moieties could undergo mechanically facilitated electrocyclic rearrangements to afford dihaloalkenes.[7] Subsequent thermal treatment (165 °C) of the olefinic products resulted in the extrusion of mineral acids (e.g., HCl). To reduce the temperature required for the elimination reaction, Moore et al. envisaged an indene-based analogue that could drive the rearrangement of the *g*DHC moieties and the elimination of HCl through aromatization (Scheme 1).



Scheme 1. Force-induced ring opening of an indene-based gDHC mechanophore (left) with subsequent HCl elimination and aromatization. The putative ring-opened intermediate is shown in brackets. PMA = poly(methyl acrylate).

To test the aforementioned hypothesis, a polymer network consisting of methyl acrylate and a bis-acrylate functionalized mechanophore cross-linker was prepared. Differential scanning calorimetry (DSC) revealed that the desired ring-opening/elimination reaction exhibited an exothermic transition starting at about 70 °C. Integration of the associated peak area enabled quantification of the number of residual *g*DHC units within the compressed material. Further efforts revealed that increasing pressures resulted in progressively lower intensity transitions (cf., 10 % *g*DHC activation was calculated at 88 MPa, whereas 20 % activation was observed at 352 MPa). Importantly, a monotonic relationship between *g*DHC activation and applied pressure was found, which indicated that the reaction was mechanically facilitated (i.e., such a relationship would not be expected for a thermal process). Additional support for a mechanochemical reaction was derived from

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[*] J. N. Brantley, K. M. Wiggins, Prof. C. W. Bielawski
University of Texas at Austin
Department of Chemistry and Biochemistry
1 University Station, A1590, Austin, TX 78712 (USA)
and
the World Class University (WCU) Program of Chemical Convergence for Energy & Environment (C_2E_2)
Seoul National University, Seoul 151-742 (Korea)
E-mail: bielawski@cm.utexas.edu

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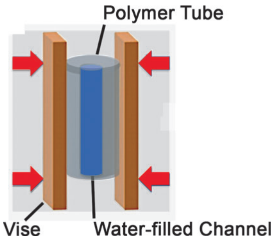
a series of control experiments. For example, a material wherein the indene-based mechanophore was not covalently attached to the polymer matrix underwent minimal activation (ca. 6%) under compression.

To verify that acidic species were generated upon compressing the aforementioned cross-linked material, a variety of analytical techniques were employed. The pH of the compressed materials was monitored with Methyl red indicator solutions or by directly measuring the acid concentration in acetonitrile suspensions of the activated polymers. The mechanophore cross-linked materials became significantly more acidic upon compression, as evidenced by a change in color for the Methyl red solution and a reduction in the measured pH (cf., pH 5.50→3.17). For comparison, minimal acid production was observed when uncompressed materials or compressed materials wherein the indene moieties were not covalently bound to the polymer matrix were examined. Aromatic C=C Raman stretches consistent with the putative anthracenyl products were also detected and further supported the proposed mechanochemical reaction.

Protic acids, however, are not the only reactive compounds that can be mechanically generated from polymeric materials. Grzybowski et al. envisioned[10] a biphasic system in which mechanically generated radicals within polymers would drive the production of hydrogen peroxide (H_2O_2) at a polymer–water interface (Scheme 2). To first test for the mechanical generation of radicals, a series of polymer tubes composed of Tygon, poly(dimethylsiloxane), or poly(vinyl chloride) were compressed in a vise. Analysis of the compressed materials using electron spin resonance spectroscopy confirmed that radicals were present, a result that was further supported by the observed bleaching of acetonitrile solutions of 2,2-diphenyl-1-picrylhydrazyl (DPPH) that were exposed to the compressed tubes. For comparison, neither resonances consistent with radical species nor DPPH bleaching were observed for virgin (i.e., uncompressed) tubes.



Scheme 2. Illustration of a polymer tube in a vise. Compression of the tube generates radicals, which react at the water–polymer interface to form H_2O_2. Red arrows indicate the direction of the applied forces (adapted from Ref. [10]).

Next, a variety of other spectroscopic and chemical methods indicated that the mechanically generated radicals could indeed form H_2O_2 under biphasic conditions when the aforementioned tubes were filled with water and then compressed. For example, upon analysis of a water aliquot removed from the compressed systems, characteristic peroxide signals were observed at $\delta = 10.1$ ppm (D_2O) and $\lambda_{max} =$ 210–300 nm by ^{1}H NMR and UV/Vis spectroscopy, respectively. A reduction wave at −0.4 V (vs. $Ag^+/AgCl$), consistent with the $E_{1/2}$ of H_2O_2, was also measured by cyclic voltammetry; likewise, a positive Fenton test (using Xylenol Orange as the indicator) was observed upon analysis of the aforementioned aliquot. Assuming all of the mechanically generated radicals ultimately formed H_2O_2, the energy efficiency for producing radicals by compression of the polymer tubes was calculated to be up to 30%.

Beyond producing H_2O_2, Gryszbowski et al. also showed that compressed materials could facilitate other useful reactions. For example, compressing tubes that were filled with aqueous solutions of Au^{III} salts resulted in the deposition of Au^0 nanoparticles on the polymer surface, as visualized by scanning electron microscopy (SEM; Figure 1 A) and other techniques. The mechanically generated peroxides could also bleach water soluble, organic dyes (e.g., Methylene Blue and Neutral Red), as determined by UV/Vis spectroscopy. In a particularly thought-provoking experiment, the oxidative cleavage of boronic esters using mechanically generated peroxides was demonstrated. Walking on a shoe injected with an aqueous solution of a boronic ester derivative of umbelliferone (which exhibited no visible fluorescence) resulted in the generation of the parent fluorophore (Figure 1 B). These results suggest that mechanically generated radicals within polymeric materials under stress could potentially contribute to mechanical failure (e.g., by inducing chemical decomposition reactions).

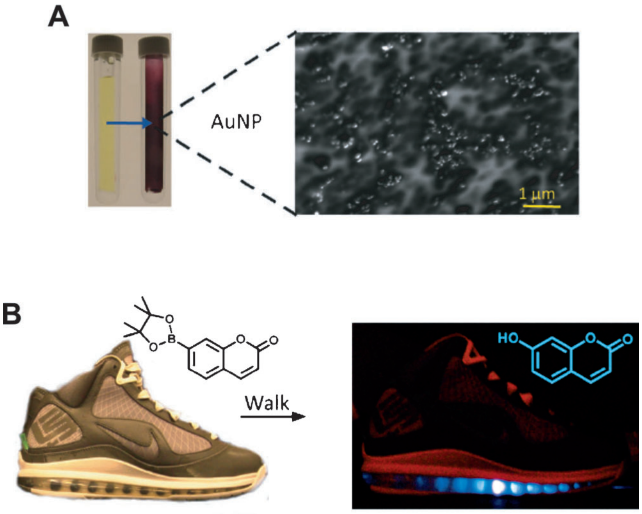


Figure 1. A) Au^{III} salts (yellow solution) were reduced to Au^0 nanoparticles (AuNP, purple solution) at a polymer interface using mechanically generated hydrogen peroxide. An SEM image of the nanoparticles is shown in the inset. B) The oxidation of a substituted coumarin to fluorescent umbelliferone was observed when a researcher walked with shoes impregnated with the former (reproduced from Ref. [10] with permission).

While Moore and Grzybowski superbly demonstrated how ingenuity within the field of polymer mechanochemistry can provide access to useful, reactive species for many applications (e.g., sensing, self-healing materials, chemical synthesis), opportunities for improvement remain. For example, the reported indene-derived materials undergo thermal activation at relatively low temperatures (ca. 50 °C), which could limit their processability. Moreover, the high pressures (more than 80 MPa) required to release HCl could restrict the applications involving these materials to extreme conditions. Additionally, higher conversions (or the development of autocatalytic cycles) are necessary for widespread use of polymer mechanochemistry in chemical synthesis. Regardless, we are confident that these reports will inspire the design of other mechanically responsive materials that generate reactive small molecules (e.g., bases, biologically active reagents, etc.) or even promote synthetically useful transformations that typically require toxic metal hydrides as radical precursors (e.g., the Barton–McCombie reaction).

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