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An outlook review: Mechanochromic materials and their potential for biological and healthcare applications

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ABSTRACT

Macroscopic mechanical perturbations have been observed to result in optical changes for certain compounds and composite materials. This phenomenon could originate from chemical and physical changes across various length scales, from the rearrangement of chemical bonds to alteration of molecular domains on the order of several hundred nanometers. This review classifies the mechanisms and surveys of how each class of mechanochromic materials has been, and can potentially be applied in biological and healthcare innovations. The study of cellular and molecular responses to mechanical forces in biological systems is an emerging field; there is potential in applying mechanochromic principles and material systems for probing biological systems. On the other hand, application of mechanochromic materials for medical and healthcare consumer products has been described in a wide variety of concepts and inventions. It is hopeful that further understanding of mechanochromism and material innovations would initiate concrete, impactful studies in biological systems soon.

1. Introduction

The interaction between molecules and mechanical stimuli takes multiple forms and results in interesting phenomenon. Scientists have used well known molecular machines and sophisticated instrumentation to probe and demonstrate the nature of interaction between mechanical stimuli and molecular response at length scales ranging from bond lengths to supramolecular and macromolecular [1]. In particular, nanoscale or single molecule force microscopy has enabled the understanding of forces involved in a plethora of molecular [2] and cellular [3–5] interactions. Amongst molecular responses towards mechanical stimuli, optical output signals possess the advantage of detection sensitivity. The installation of fiber optical sensors is also less intrusive and can be tolerated by a wide variety of environmental conditions [6]. Molecules or material systems that change their optical properties with the application of a mechanical stimulus are termed mechanochromic. The change is often manifested as a change in transmitted or emission wavelengths (color), sometimes also changes in emission intensity and lifetime, upon irradiation with an excitation light source in the ultraviolet or visible. Mechanochromism arises from one or more of a number of phenomena in which light interacts with the molecular systems from a single molecule to supramolecular length scales. The most common mechanisms are summarized in Table 1. They will be described in more details in the respective sections that follow.

The need to assess material mechanical integrity is fairly ubiquitous. Coupled with the ease and high sensitivity of capturing optical output signals, mechanochromic materials hold somewhat obvious promises as sensing agents. For example, mechanochromic polymers are immediately relevant towards monitoring failure and fracture in the bulk materials. On the other hand, the relevance of mechanical perturbation sensing to biological systems has just recently garnered enough specialized research interests to achieve salient perspectives [7]. Traditionally, it is known that key indicators of human and animal health involve mechanical properties of organs. For example, blood pressure depends on the mechanical properties of blood vessel walls [8]. Hair cells and hair bundles in the mammalian cochlea region interact with acoustic perturbations [9]. Small mechanical stimuli has been known to promote tissue growth [10,11]. Currently, the emerging field of mechanobiology specifically studies molecular mechanisms when cells interact with mechanical signals. The traction forces and trajectory of mechanically active cells are monitored through movement and adhesion processes with force microscopy conducted on mechanoresponsive (but not necessarily optically active) surfaces that mimic extracellular matrices. For example, surfaces of micropillars fabricated from poly(dimethylsiloxane) [12,13], have been used extensively in cellular studies. On the molecular level, the aggregation and accumulation of cellular proteins could take place through sensing mechanical perturbations in the plasma membrane [14]. For such studies, methods involving traditional fluorescence marker are employed. Overall, the direct employment of mechanochromic materials for mechanobiology studies is next to non-existent.

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Table 1
Main mechanisms of mechanochromism in materials.

	Mechanism	Examples
1	Rearrangement of bonds	Change in E–Z conformation; breaking of C – O bonds in spiropyran; stressing of polydiacetylene systems
2	Forming or breaking dye aggregates	Grinding or smearing small molecule dyes such as oligo-phenylene vinylene, and perylene; and straining elastomers containing a dispersion of these small molecule dyes.
3	Change of photonic pathlengths	Alternating polymeric lamellae constructed from block copolymers

Descriptions of mechanochromic materials for biomedical and healthcare applications, on the other hand, flourish in the patent literature. Stress and strain exerted by the human body on external environment can be measured and monitored, through personal care devices containing mechanochromic components, to analyze body motion for orthotics. Certain material systems, such as functionalized polydiacetylenes, are versatile and had been described for their potential incorporation in consumer products with diverse functionalities. Biological reagents of medical significance could be captured by a functionalized mechanically responsive surface in vitro, inducing mechanical perturbations that transduce to optical signals.

This review aims to describe mechanisms underlying mechanochromism exhibited in examples of common material systems. The classification of these mechanisms is listed in Table 1. The review shall connect these materials' properties, wherever possible, with reported and potential applications in biology and healthcare. It should hopefully serve as a pointer towards how existing materials could be applied and how future materials could be designed. It is to be noted that certain other elegant systems engineered to generate optical output from mechanical inputs of biological systems are not included. For example, substrates in cell mechanics studies were incorporated with FRET donor–acceptor dyad molecules; the changes in the donor–acceptor distances arising from cell movement-induced deformation changed the emission patterns [4,5]. These systems did not describe materials that would show an intrinsic propensity to optically respond to mechanical inputs, whether in terms of changes in molecular structure, arrangement or material architectures. These systems are therefore not included in this review. Neither are nanoparticles and nanocomposites described singly as a class of mechanochromic materials. Aggregation behavior of colloids is known to be affected by shear [15]. Nanoparticles, such as ligand-functionalized gold [16], indeed exhibit aggregation-based chromic behavior in solution or in suspension (albeit not from direct mechanical perturbation). The mechanisms involved can be explained with the various nanometer length-scale mechanisms listed in Table 1, and are not further elaborated. There is also a current dearth of reports that explicitly linked chromic transitions to macroscopic application of force on solutions or encapsulated systems. (It's to be noted that concepts have been mentioned in patent literature for the fabrication of biocompatible nanoparticles from mechanoluminophores, and dispersion in vivo to sense mechanical perturbations therein [17].)

2. Rearrangement of bonds

Molecular bonds can be broken and rearranged on mechanical duress. Recent reviews and studies have scrutinized the nature of bonds that are susceptible to activation by macroscopic straining or ultrasonic irradiation, and the order of magnitude of the forces involved in these processes [18–20]. Mechanically activated reactions that also change the optical properties of the mechanophore, before and after bond-breaking, give rise to mechanochromism. Applications to biological systems for a few examples of such mechanophore-containing mechnochromic materials have been cited in the patent literature. Remarkably, diacetylenes, a class of synthetically versatile conjugated molecules, have shown much utility in optical sensing for a large variety of biological systems and consumer product inventions. Representative structures of diacetylenic monomers, together with polymerization methodologies are shown in Scheme 1.

First studied in the 1980s, researchers since have been able to tune the properties and processability of polydiacetylenes (PDAs) through chemical functionalization [21,22]. Importantly, PDAs can be readily cross-linked with UV light, causing an effective change in its conjugation length and, in turn, its optical properties [23]. On the other hand the cross-linking or 1,4-cyclo-addition reaction can be induced by the application of stress [22,24–26]. The un-crosslinked phase is known as the non-fluorescent "blue phase", and the cross-linked product forms a fluorescent "red phase" [27].

Polydiacetylenes have shown remarkable utility as a substrate for biomolecule immobilization and subsequent detection of the counterpart analyte [21,28]. Example of analytes include various types of proteins and antigens. Diacetylene or PDA vesicles are immobilized on functionalized substrates through covalent or non-specific linkages. The mechanism for subsequent biosensing has been suggested to involve pressure exerted by the mass of bound analyte. This then causes a change in conformation of the conjugated backbone of the PDA vesicles [28], turning on the red fluorescence. Analytes to which a functionalized PDA biosensor is potentially applicable are depicted in Scheme 2. Many inventions have been built based on claims on the sensing of a variety of biomarkers [29,30].

Diacetylene attached with long alkyl chains could be functionalized with an amine headgroup to form ambipolar molecules [31,32]. These lipids self-assemble into nanotubes that show chromic changes when bacteria were deposited (PDA's ability to kill bacteria has also been demonstrated in this study and elsewhere [29]). Cross-linked PDA lipids have also been disclosed to self-assemble into ribbons and sheets [33]. These non-fluorescent structures insert into lipid bilayers. Disruption to the PDA conformation and turning on of fluorescence could potentially detect conformational changes in membranes, including important membrane activities and functions such as structural disruptions, transmembrane signaling and enzyme activities.

A large amount of patent literature highlighted PDA's potential utility in mass-market consumer products for healthcare. A deformation-induced change in color, when incorporated into garments for example, can be used to measure pressure exertion from various body parts and diagnose body movements. Bowlin et al. described the fabrication of a PDA-containing polyurethane polymer for shoe soles, such that the distribution of strain exerted by the feet could be evaluated [34]. The invention also describes the potential for such elastic materials to be incorporated in tight-fitting clothing, such as pantyhose and sportswear, and characterizes joint movement. Ribi et al. outlined the fabrication of a soft color-changing dental night guard device blending thermoplastics such as polyvinyl acetate with powdered PDA [35]. Mechanochromic and thermochromic PDA-containing polymers could also act as a deformation and temperature history indicator for food product, when incorporated in food packaging materials [36]. Change in temperature and mechanical pressure that occurred at any point of time during processing and storage of perishable food products could be registered by individual food packaging material containing stimuli-responsive components. The quality of the perishable contents could then be quickly and optically assessed on-the-spot by consumers.

In contrast to the traditional PDA system, in which the exact mechanisms of topochemical reactions are not well understood, recent examples of mechanophore-containing polymers consist of structurally-defined molecular systems [37–39]. The impact of macroscopic straining or shear forces from sonication cavitation on chemical bonds has been the subject of much investigation [19]. Moore et al. demonstrated the rupture of the C – O bond in spiropyran tethered to polymethylmethacrylate (PMMA) chains, when the bulk polymer was strained [39,40]. The product of mechanically induced reaction is a red merocyanine dye as compared to the colorless spiropyran (Scheme 3). Such a system inspired the engineering of a variety of mechanophore-centered polymers [41].