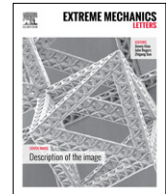




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Computational investigation of shear driven mechanophore activation at interfaces

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ABSTRACT

Self-healing and self-reporting interfaces can alleviate damage related costs for both coatings and composites. In this paper we propose to utilize molecular units termed mechanophores, that undergo productive chemical transformations in response to force, to augment interfaces with self-healing and self-reporting functionality. We investigate the critical parameters for mechanophore-functionalized interfaces by building two computational models: a kinematic model with rigid non-interacting walls forming the interface and a molecular dynamics model with substrates of Lennard-Jones particles. In both the models the mechanophore is idealized as a coarse grained two-bead system governed by a double-well potential that emulates a force directed chemical reaction. Subjecting the interface models to shear, our study reveals that mechanophores progressively activate as interfacial displacement increases starting with the mechanophores aligned along the direction of shear. Subsequently we find that activation happens only if the bonds attaching the mechanophores to the substrates are strong enough to transmit the force necessary to activate the mechanophore. When substrates forming the interface are adhesive, the transmission of shear is delayed, in turn delaying activation of mechanophores. Adhesion-based changes in the conformation of the interface alter the extent of mechanophore activation. These results are a first step towards designing mechanophore-enabled self-reporting and self-healing composites and coatings.

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1. Introduction

Solid interfaces are prevalent both within materials and structures. Some ubiquitous examples include nanoparticle polymer composites [1], fiber-reinforced composites [2], and polymer coatings [3–5]. Interfaces with self-reporting [6–8] and autonomous self-healing [9,10] capabilities help manage damage and lower life cycle costs. The self-reporting approach provides a localized indication of the extent of damage and the autonomous self-healing approach provides localized repair at the site of damage mimicking biological systems. In this work

we propose to augment interfaces with mechanochemical functionality by bonding force triggered chemical units (termed mechanophores) [11] at the interface of two substrates. Several mechanophores have been developed that are promising for self-reporting and self-healing, including spiropyran that changes color [12], bis(adamantyl)-1,2-dioxetane that luminesce [13], gem-dichlorocyclopropanated indene that releases an acid [14], gem-dibromocyclopropane that triggers cross-link formation [15,16] and olefin metathesis catalyst with two tightly bound N-heterocyclic carbene ligands triggers polymerization of monomers or forms cross-links [17].

This paper is focused on mechanophore triggering at a sparsely populated interface subjected to shear loading. This focus on triggering intentionally neglects the chemical details that would be associated with a particular

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Table 1

The extremal values for the cubic Bezier of the double-well and the parameters for the Morse and the Lennard-Jones potentials.

Double-well cubic Bezier			
	Minima 1	Minima 2	Maxima
Distance (Å)	7.03	13.19	11.89
Potential (kcal/mol)	-55.37	-55.30	-1.69
Morse potentials			
	Double-well	Attachment	
D (kcal/mol)	61.03	50.79	[8, 140]
α (Å ⁻¹)	0.17	0.36	[0.2, 1.4]
r_0 (Å)	7.69	13.73	4.0
Range (Å)	(0, 4.67)	(15.08, ∞)	-
Lennard-Jones potentials			
	Substrate-mechanophore	Intra-substrate	Inter-substrate
ϵ (kcal/mol)	1.23	12.31	6.16
σ (Å)	3.12	2.57	5.14
n (Å ⁻³)	0.06	0.06	-

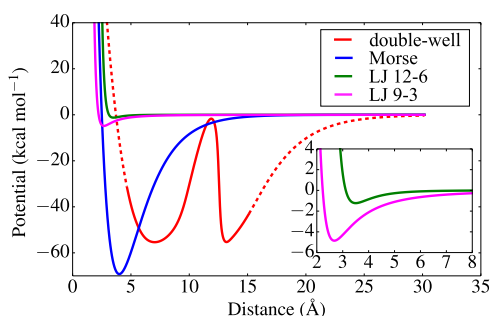


Fig. 1. Representative plot of potentials used in kinematic and MD simulations. The mechanophore double well potential is stitched from a cubic Bezier curve (—) flanked by two Morse potentials (- - -). Inset: Zoomed in view of the nonbonded interactions near the well. Note that the LJ 9-3 potential is deeper than the corresponding LJ 12-6 potential.

self-healing or self-reporting reaction in order to ascertain general design guidelines. We develop both a kinematic model and molecular dynamics model with coarse grained mechanophores and representative substrates. These models are used to interrogate the percentage of mechanophores activated as a function of interfacial displacement for different degrees of interactions between the mechanophore and substrate. Furthermore we examine how the presence of ambient temperature and adhesive interfacial conditions affect activation.

2. Methods

To build a model that captures mechanophore activation due to interfacial shear, we begin with a representative mechanophore and its interactions with a substrate. The mechanophore is simplified to two coarse grained beads bonded together. This bond is captured as a double-well potential that models a reversible isomerization reaction with bond length change. This 1D potential model inspired by first principle steered molecular dynamics studies of mechanophores [18,12], assumes that the entire reaction can be mapped onto a single reaction coordinate

and that the force directed chemical reaction takes this same reaction pathway [19]. The double well potential captures the basic physics seen across mechanophores: with applied force the energy barrier for the forward reaction is lowered and the energy barrier for the reverse reaction is increased (supporting information Section 1.2). To construct the potential (Fig. 1) two Morse potentials (Eq. (1)) were stitched together with a Bezier cubic spline (supporting information Section 1.1). The Bezier cubic spline and the Morse potential values were chosen to obtain extremal energy values (Table 1) in the range of those from quantum mechanical calculations of the mechanophore spiropyran [12]. A mechanophore is termed open (activated) if the bond length is greater than the position of the second potential minima and is termed closed otherwise.

Each bead of the mechanophore is covalently bonded to a substrate. The covalent substrate attachment is modeled with a Morse potential that captures the anharmonicities of the bond away from equilibrium [20] and the dissociation of the bond [21] with a finite energy. The Morse potential V^{Morse} as a function of bond length r is

$$V^{\text{Morse}} = D \left[e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)} \right] \quad (1)$$

where r_0 is the bond length, D is the energy required to break the bond, and α is inversely proportional to the half-width of the potential well. The bond stiffness (k^{Morse}) of the bond at r_0 is directly related to α and D :

$$k^{\text{Morse}} = 2\alpha^2 D. \quad (2)$$

The half-width $w_{1/2}^{\text{Morse}}$ is defined as the distance from the equilibrium point r_0 at which the applied force dV^{Morse}/dr is maximum ($F_{\text{max}}^{\text{Morse}}$). The maximum force and half-width are related to the Morse potential parameters by:

$$F_{\text{max}}^{\text{Morse}} = \frac{\alpha D}{2} \quad (3)$$

$$w_{1/2}^{\text{Morse}} = \frac{\ln(2)}{\alpha}. \quad (4)$$

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