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Percolation modeling of self-damaging of composite materials

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HIGHLIGHTS

- We propose the concept of autonomous self-damaging in “smart” composite materials.
- Percolation model is used to study the onset of the initial material’s fatigue.
- Numerical Monte Carlo simulations of the connectivity and conductance are reported.
- We seek a sharp drop in the integrity of material at a certain level of fatigue.
- Sophisticated structure is required involving not only self-damaging, but also self-healing.

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ABSTRACT

We propose the concept of autonomous self-damaging in “smart” composite materials, controlled by activation of added nanosize “damaging” capsules. Percolation-type modeling approach earlier applied to the related concept of self-healing materials, is used to investigate the behavior of the initial material’s fatigue. We aim at achieving a relatively sharp drop in the material’s integrity after some initial limited fatigue develops in the course of the sample’s usage. Our theoretical study considers a two-dimensional lattice model and involves Monte Carlo simulations of the connectivity and conductance in the high-connectivity regime of percolation. We give several examples of local capsule–lattice and capsule–capsule activation rules and show that the desired self-damaging property can only be obtained with rather sophisticated “smart” material’s response involving not just damaging but also healing capsules.

1. Introduction

There has been an increasing recent interest in “smart materials” which utilize nanoscale features to achieve useful properties, such as self-healing [1–11]. For example, in such materials development of damage and fatigue can be delayed by embedded capsules containing a microcrack-healing agent activated by a “triggering” mechanism [11]. In the present work we extend this concept to materials with self-damaging properties [12,13], as will be explained shortly, as well as to situations when both mechanisms are utilized. The first autonomous self-healing of polymer composites was realized [3] with the polymerization process initiated by the released healing agent preventing the propagation of cracks caused by mechanical stress. This finding was followed by interesting experimental [1,2,5,7,14–24] and theoretical [4,6,8–11,25–29] developments. Earlier successful approaches to self-healing required an external trigger by mechanical, physical, or chemical means [30–33].

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A promising new application of smart-materials concepts could be in developing "self-damaging", also termed self-destructive, self-deteriorating, or transient materials. The first experimental realization of this property at the materials level has recently been reported for transient electronics [12,13]. Such concepts can be beneficial in many applications. They are in fact already utilized in medicine, e.g., commercially sold single-use syringes, fabrication of complex-shaped objects (self-destructive core mold materials for metal alloys [34]), as well as commercially available self-decomposing tags, labels and plastic bags. However, similar to self-healing these earlier realizations have involved activation by external mechanical, physical (such as high temperature or laser illumination), or chemical means, rather than being internally driven by the materials' properties.

One important avenue of research has involved achieving smart-materials response at the nanoscale [4,6,7,10,11,35]. The reason for this has been that such material designs promise to allow control of the material's fatigue at the earliest stages of its development, when damage is not yet macroscopic. Material degradation [36] ultimately results in formation of voids and cracks that are macro-objects. These are initiated by the development of microscopic crazes and microcracks, the growth of which can be prevented (for self-healing) or accelerated (for self-damaging) at the nanoscale.

In this work we use a percolation modeling approach earlier utilized for self-healing [4,10,11], which considers probabilistic bond breakage in a lattice model, offering a microscopic statistical–mechanical description of the time-dependent material fatigue evolution, controlled, for instance, by releasing a "glue" substance from nanoporous capsules (in self-healing experiments [11] these were nanoporous fibers). Here we instead consider capsules causing self-damaging, as well as their combined effect with those causing self-healing. Damage formation is a multiscale phenomenon [37,38], and its modeling at different scales requires various approaches. These include continuum rate equation approach [25], as well as other continuum descriptions [29,36] involving consideration of free energies of tensile cracks or crack surface energies. More microscopic approaches include molecular-level modeling [29,39], discrete element methods [29], and the aforementioned "atomistic" percolation model [4,10,11] which could be suitable for understanding of certain aspects of self-healing and self-damaging at the nanoscale.

Microscopic statistical–mechanical modeling cannot always be directly related to macroscopic material's parameters, but it allows us to explore patterns of possible behaviors involving really atomic-scale effects. Here we are interested in the degree of complexity and local correlations required of the damaging (and healing) capsule activation kinetics to ensure a relatively sharp, well pronounced drop in the materials integrity after some initial fatigue developed due to the sample's usage. We use the two-dimensional (2D) lattice model earlier developed for self-healing [4], involving Monte Carlo (MC) simulations of the connectivity as a measure of the overall material's integrity. Furthermore, the actual macroscopic material's properties are typically nonlinear in the microscopic morphology measures [37], and therefore, as an example, we consider the behavior of the sample's conductivity. We point out that electrical transport properties are among the important experimentally studied macroscopic indicators of both self-damaging [12] and nanoscale self-healing [35], the latter also used as a probe of the sample's integrity. Various transport properties depend on and have been used as indicative of the material's integrity, for example, thermal conductivity [40,41], photoacoustic wave propagation [42,43], and of course electrical conductivity [35,44–47].

In addition to self-damaging, our statistical–mechanical percolation-model approach could be of interest in studies of actual networks' functionality, especially when active response/control is desired. Indeed, similar ideas involving concepts related to self-healing [48,49] and self-damaging [50] have been considered in the *sensor*-network design literature. Self-damaging concepts can be useful, for example, in designs aimed at abruptly shutting a whole computer or sensor network down if enough interconnected nodes are compromised. We point out, however, that both for materials fatigue kinetics and other applications, we are interested in self-damaging (aggressive "shutdown") after the initial, limited damage to the network or material, when the latter are still largely intact. Therefore, here we *do not consider* the critical-point behavior regime near the percolation transition, which has been of interest [51–53] in many studies of percolation models, because we are only interested in the regime of relatively high connectivity, as further commented on later. Details of our model and numerical approach are described and illustrated in Section 2. Section 3 presents results for more complicated dynamical rules. Finally, Section 4 offers a concluding discussion.

2. Percolation model of self-damaging

In this section we present the percolation model used in our study of features of material self-damaging with and without self-healing. Our MC simulations were carried out for a 2D lattice model similar to that which in earlier studies allowed exploration of aspects of self-healing [4,10,11]. We use a square lattice of N^2 sites, with periodic boundary conditions. System's degradation due to damage is described by the process of random breakage of bonds connecting these sites, as detailed shortly. Some randomly positioned sites have special properties corresponding to damage-inducing or healing inclusions (capsules) in the material. The "capsule" sites can be activated and affect the kinetics of the bond connectivity in the system according to the rules defined below, as is illustrated in Fig. 1.

Initially, the lattice is fully connected. We assume that during the "use" of the material, fatigue (initial damage) sets in. Here it is modeled by random breakage of bonds. Simulation time, t, is measured in units of MC sweeps (MC steps) through the system: $2N^2$ random bond breakage attempts are carried out per each such time step. Each attempt selects a bond randomly, and, if it is intact, then it is broken with small probability p. Here we took the value

$$p = 0.01, \tag{1}$$