Harnessing biomimetic catch bonds to create mechanically robust nanoparticle networks

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A B S T R A C T

Using computer simulations, we investigate the mechanical properties of a network of polymer-grafted nanoparticles (PGNs) that are interlinked by labile "catch" bonds. In contrast to conventional "slip" bonds, the life time of catch bonds can potentially increase with the application of force (i.e., the rate of rupture can decrease). In effect, the bond becomes stronger under an applied force (if the strain rate is sufficiently high). Subjecting the PGN networks to a tensile deformation, we find that the networks encompassing catch bonds exhibit greater ductility and toughness than the networks interconnected by slip bonds. Moreover, when the applied tensile force is released, the catch bond networks exhibit lower hysteresis and faster relaxation of residual strain than the slip bond networks. The effects of the catch bonds on the mechanical behavior are attributed to transitions between two conformational states, which differ in their sensitivity to force. The findings provide guidelines for creating nanocomposite networks that are highly resistant to mechanical deformation and show rapid strain recovery.

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1. Introduction

One of the vital components in materials that can withstand significant strain without undergoing catastrophic failure is reactive, labile chemical bonds, which readily reform once they are broken [1,2]. This concept lies at the heart of such materials as dual cross-linked polymer-grafted nanoparticle (PGN) networks [3–7]. These materials encompass nanoparticles that are decorated with end-grafted polymers. The free ends of these polymers contain reactive groups that form bonds with reactive groups on neighboring chains. Some fraction of these bonds are labile connections and the other fraction are less reactive, higher strength "permanent" bonds, which do not reform after being broken. Due to the presence of both the labile and permanent bonds, the material is referred to as a "dual cross-linked" network. Using computational modeling, we showed that when this network is subjected to a tensile deformation, the labile bonds allow the nanoparticles to "reshuffle" by forming bonds with new neighbors as connections with previous partners are broken [7]. This reshuffling allowed the network to undergo a degree of self-healing even as the material was strained and in this manner, the dual cross-linked PGNs displayed remarkable ductility and strength. Hence, the presence of the labile bonds led to an improvement in the mechanical robustness of the material.

In the previous studies [3–8], the labile bonds were modeled as traditional "slip" bonds [9], where the lifetime of the bond decreases with an applied tensile force. There is, however, a class of non-covalent chemical bonds, known as "catch" bonds [10–20], where the bond lifetime increases with force. On a conceptual level, catch bonds behave much as the finger trap toy; the harder you pull, the more tightly your fingers become bound by the encasing cylindrical tube [18]. Catch bonds play a crucial role in biological processes [11–20], especially in the binding of leukocytes to the extracellular matrix [11–15]. Recently, there has been an effort to synthesize small molecules that exhibit catch bond behavior [21,22].

In the ensuing study, we examine the properties of PGN networks where the particles are interconnected by labile catch bonds, as shown in Fig. 1. Given that the catch bonds become stronger with an applied tensile force, we hypothesize that a PGN network involving these bonds will exhibit unprecedented resistance to deformation. We also anticipate that the catch bonds will enable the network to display significant self-healing behavior. To test these hypotheses, we undertake the simulations described below, where we adapt our previous model for the PGN networks [3–8] to include the catch bonds. Using this new model, we determine the

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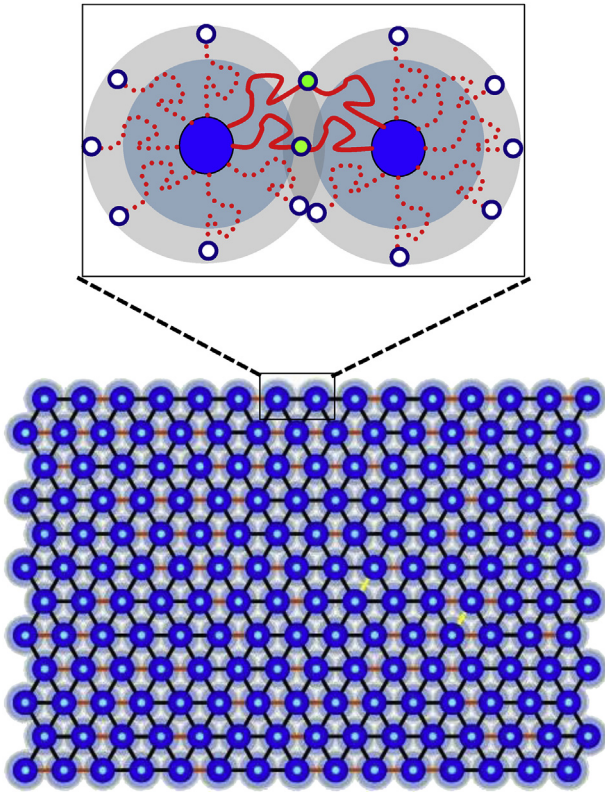
Fig. 1. Polymer grafted nanoparticles (PGNs) consist of a rigid core (drawn in dark blue) and a corona of end-functionalized polymers. (To highlight the chain ends, the region encompassing these ends is indicated in the lightest shade.) With the overlap between neighboring coronas, the reactive end groups can form labile or permanent bonds (indicated in green) that connect the polymer arms (in solid red) and thus, link the particles. PGNs interlinked by both labile and permanent bonds form a dual cross-linked nanoparticle network. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

response of the system to mechanical deformation and contrast the behavior of systems interconnected by slip bonds to those that are bound by the catch bonds. As we show below, the catch bonds do indeed provide new opportunities for creating composites with an exceptional response to applied tensile forces, including self-healing properties and low hysteresis as the material is repeatedly subjected to loading and unloading of the force.

We start by detailing our approach and relating our simulation parameters to physical experimental values. We then analyze the response of the system to varying levels of strain, as well as multiple cycles of mechanical deformation. We emphasize that to date such materials have not yet been synthesized, and hence, these predictions can prove useful in creating a new class of mechanically robust nanocomposites.

2. Methodology

The fundamental unit in our system consists of a spherical, rigid nanoparticle of radius r_0 that is decorated with end-grafted polymers, which form a corona around the particle. The corona chains are in the semi-dilute regime and assumed to be in a good solvent; the thickness of the corona is given by $H = qr_0$. In the ensuing discussion, all the length scales in the system are given with respect to the core radius r_0, and hence, we consider a polymer-grafted nanoparticle (PGN) of core radius unity and a corona thickness q.

The ends of the corona chains encompass reactive groups and the reactive groups on the neighboring PGNs interact to form either a strong ("permanent") or a labile bond (see Fig. 1). By means of these bonds, the PGNs are cross-linked into a swollen network. Both the permanent and labile bonds can rupture, but the only labile bonds can reform after they have ruptured.

In this coarse-grained approach, we model the interaction between two PGNs by a sum of interaction potentials: $U_{int} = U_{rep} + U_{coh} + U_{link}$. The term U_{rep} characterizes the repulsive interactions between the coated nanoparticles and is given by Ref. [23]:

$$\frac{U_{rep}(R)}{k_B T} = \frac{5}{18} f^{3/2}$$
$$\times \begin{cases} -\ln(R/\sigma) + \left(1 + f^{1/2}\big/2\right)^{-1}, & R \leq \sigma \\ \left(1 + f^{1/2}\big/2\right)^{-1}(\sigma/R)\exp\left[-f^{1/2}(R-\sigma)\big/2\sigma\right], & R > \sigma \end{cases}$$

$$(1)$$

Here, f is the number of arms, R is the center-to-center interparticle separation and $\sigma = 2(1+q)(1+2f^{-1/2})^{-1}$ is the range of the potential [24,25]. The attractive cohesive interaction between the coated nanoparticles is described by a pseudopotential U_{coh}, which is constant for small values of R and balances the repulsion at the corona edges to allow for overlap between neighboring coronas. This potential is chosen to have the following form [26]:

$$U_{coh}(R) = -C\{1 + \exp[(R-A)/B]\}^{-1},\qquad(2)$$

where C is an energy scale, and A and B are length scales that determine the respective location and width of the attractive well in the potential.

The term U_{link} describes the attractive interaction between two particles linked by the bonded polymer arms. The attractive force acting between two bonded particles is given by Ref. [7]:

$$F_{link}(r) = N_b \kappa(r) r,\qquad(3)$$

where N_b is the number of bonds formed between the given pair of particles, and $\kappa(r)$ is the spring stiffness, which increases progressively with the chain end-to-end distance $r = R - 2$. We use the following equation, obtained for a worm-like chain [27], to calculate $\kappa(r)$:

$$\kappa(r) = k_B T R_0^{-2}\left(1 + 2\left[1 - r^2(2L)^{-2}\right]^{-2}\right).\qquad(4)$$

Here, $2L$ is the contour length of the chain formed by bonding two polymer arms of length L, $R_0^2 = 4l_p L$ is the mean-square end-to-end distance of the latter chain, and l_p is its persistence length. The value of N_b in Eq. (3) depends on the extent of overlap between the coronas of the nanoparticles, and on the kinetics of bond formation and rupture [3,7].
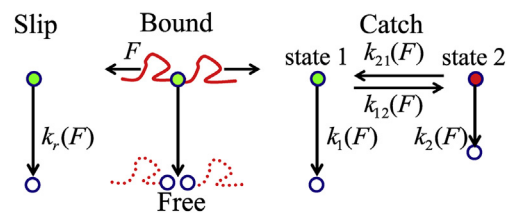
Fig. 2. Rupture of the slip and catch bonds. Slip bonds have one bound state; the bond rupture rate is given by $k_r(F)$, which depends on the force F. Catch bonds have the two bound states, state 1 and state 2; the respective rupture rates are given by $k_1(F)$ and $k_2(F)$. Rate constants for the transitions between the bound states, $k_{12}(F)$ and $k_{21}(F)$, are also force-dependent.