Supplementary Information for

A catch bond mechanism with looped adhesive tethers for self-strengthening materials

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Theoretical Considerations

In this section we present derivations of the lifetimes of tether dissociation events using probability theory and kinetic theory. In the main text, we have defined adhesin dissociation rate r_A (Eqn. 2) and loop opening rate r_L (Eqn. 3), which we will refer in this text extensively. Note that at a constant pulling force, these rates will be constant and do not depend on time. In our derivations, we made three notable assumptions to simplify the analysis. In our design, the tethers are short, therefore we don't explicitly consider the effect of the entropic elasticity of the tethers. Second, since tether I is slack and under no force initially, we discounted the possibility of tether I adhesin dissociating before dissociation of tether II adhesin or loop opening events. Third, our theory did not consider rebinding of the interactions, which is only true if the forces and distances are large enough to render the rebinding probability negligible. We note that in our MD simulations, these conditions are not enforced, and this may affect the characteristics of lifetime curves. For instance, rebinding events indeed occur and this does have a minor effect on lifetime curves (discussed in the section entitled *Effects of rebinding on the lifetime curve* in the Supplementary Information). Nevertheless, the main arguments with regards to catch bond existence and scaling trends are in good agreement with what's predicted by theory.

In the main text, we have established that the probability of adhesin dissociation before loop opening dictates the which failure path the event will follow. In larger sample sizes, $P_{A<L}$

fraction of events will fail sequentially and will have a mean lifetime $\langle\tau\rangle_S$. On the other hand $1 - P_{A<L}$ fraction of events will fail in a coordinated fashion and will have the mean lifetime $\langle\tau\rangle_C$. Therefore, the average lifetime of the system will have a form of

$$\langle\tau\rangle = P_{A<L}\langle\tau\rangle_S + (1 - P_{A<L})\langle\tau\rangle_c \tag{S1}$$

In sequential failure, the adhesin of tether II dissociates (event S_1), which is followed by dissociation of the adhesin of tether I (event S_2). In coordinated failure, the loop opens, C_1, which is followed by dissociation of one of the adhesin that are sharing the load, C_2, and dissociation of the remaining adhesin, C_3. We will define and calculate each individual event lifetimes depicted in Figure S1 to calculate sequential lifetime $\langle\tau\rangle_S$ and coordinated failure lifetime $\langle\tau\rangle_c$.

Probability of adhesin dissociation prior to loop opening $P_{A<L}$

According to probability theory $P_{A<L}$ after time *t* can be defined as

$$P_{A<L} = \int_0^\infty P(L > t|A = t)P(A = t)dt \tag{S2}$$

where A and L are the lifetimes of adhesin dissociation and loop opening events respectively. Here, we have a product of a conditional probability of 'loop opening occurs after time *t* given that adhesin dissociation occurs at time *t*' and the absolute probability of 'adhesin dissociation occurs at time *t*'. These two events are independent from each other, i.e., the dissociation of the adhesin does not affect the opening of the loop. Thus, Eqn. S2 can be written as

$$P_{A<L} = \int_0^\infty P(L > t)P(A = t)dt. \tag{S3}$$

To solve Eqn S3, we will derive $P(L > t)$ and $P(A = t)$ separately. The master equation for evolution of loop interaction involves the net of unbinding, which is governed by $r_L(f)$, and rebinding transitions of the loop. Since the rebinding is negligible, this equation will have the form

$$\frac{dP(L > t)}{dt} = -r_L(f)P(L > t). \tag{S4}$$

When we rearrange Eqn. S4, we get

$$\frac{dP(L > t)}{P(L > t)} = -r_L(f)dt. \tag{S5}$$

Next, we integrate both sides of Eqn. S5:

$$\int_0^{P(L>t)} \frac{dP(L>t)}{P(L>t)} = \int_o^t -r_L dt \tag{S6}$$

Thus $P(L > t)$ is found to be

$$P(L > t) = e^{-r_L(f)t}. \tag{S7}$$

On the other hand, $P(A = t)$ can be calculated from the derivative of cumulative probability distribution function, Φ, which is the probability of adhesin to break before time t, $P(A < t)$. We can follow the same methodology for the adhesin dissociation and use S4-S7 to find

$$P(A > t) = e^{-r_A(f)t}. \tag{S8}$$

Since $P(A < t)$ is $1 - P(A > t)$, the cumulative probability distribution function, Φ will be

$$\Phi = 1 - e^{-r_A(f)t}. \tag{S9}$$

Therefore, the probability of adhesin dissociating at time t is written as

$$P(A = t) = \frac{d\Phi}{dt} = \frac{d}{dt}\left[1 - e^{-r_A(f)t}\right] = r_A\, e^{-r_A(f)t}. \tag{S10}$$

Plugging in Eqn S7 and S10 in S3, we get

$$P_{A<L} = \int_0^\infty r_A e^{-(r_L(f)+r_A(f))t} dt = \frac{r_A(f)}{r_L(f)+r_A(f)}. \tag{S11}$$

Lifetime of the initial dissociation event of the system

In our system, the first event will either be S_1 or C_1. We denote their lifetimes as $\langle\tau\rangle_{S_1}$ and $\langle\tau\rangle_{C_1}$. In both cases, the system starts from an initial state, i.e., tether II adhesin is intact and loop is closed. Note that loop and adhesin interactions are serially connected. Even though S_1 and C_1 result in two different failure modes, they both represent transition to a new state. The probability of the transition will be the multiplication of probabilities of interactions to remain intact, since S_1 and C_1 are independent events:

$$P_{Tr} = P(A > t) \cdot P(L > t) \tag{S12}$$

Since we derived $P(A > t)$ and $P(L > t)$ in Eqn S7 and S8, Eqn S12 can be written as

$$P_{Tr} = e^{-(r_L(f)+r_A(f))}. \tag{S13}$$

Mean lifetime (expected value), $\langle\tau\rangle$, is calculated from probability distribution $\rho(t) = \frac{dP}{dt}$ as

$$\langle\tau\rangle = -\int_0^\infty t\, \rho(t) dt. \tag{S14}$$

By plugging in S13 in S14, we can calculate the transition lifetime to be

$$\langle\tau\rangle_{S_1} \text{and } \langle\tau\rangle_{C_1} = \int_0^\infty (r_L(f) + r_A(f)) e^{-(r_L(f)+r_A(f))t} t dt = \frac{1}{r_L(f)+r_A(f)}. \tag{S15}$$

Lifetime of sequential failure events $\langle\tau\rangle_S$

After S_1, load transfers to tether I and the surfaces remain connected until tether I adhesin dissociates, S_2. Using Eqn S14 and S8, $\langle\tau\rangle_{S_2}$ is calculated as

$$\langle\tau\rangle_{S_2} = -\int_0^\infty e^{-r_A(f)t}\, t\, dt = \frac{1}{r_A(f)}. \qquad \text{(S16)}$$

Since the lifetime of sequential failure $\langle\tau\rangle_S$ is the sum of lifetimes of the events S_1 and S_2, it can be written as

$$\langle\tau\rangle_S = \langle\tau\rangle_{S_1} + \langle\tau\rangle_{S_2} = \frac{1}{r_A(f)} + \frac{1}{r_A(f)+r_L(f)} \qquad \text{(S17)}$$

Lifetime of coordinated failure events $\langle\tau\rangle_C$

After the loop opening event C_1, the load is shared between the adhesins as both tethers become stretched. The adhesin dissociation rate function in this case will be $r_A(f/2)$ since each tether will be carrying half of the load. The lifetime of dissociation of one of the adhesins $\langle\tau\rangle_{C_2}$ can be calculated from probability of both adhesins to remain intact P_{II}, which is the product of probability of two tethers to remain intact:

$$P_{II} = e^{-r_A(f)t} \cdot e^{-r_A(f)t} = e^{-2r_A(f)t}. \qquad \text{(S18)}$$

Using Eqn S14, we determine $\langle\tau\rangle_{C_2}$ to be

$$\langle\tau\rangle_{C_2} = \int_0^\infty 2r_A e^{-2r_A(f/2)t} = \frac{1}{2r_A(f/2)}. \qquad \text{(S19)}$$

Note that Figure S1 depicts the scenario where tether II dissociates before tether I. It is equally likely that tether I can break before II, however, since the adhesins have the same dissociation rate, both cases will result in the same lifetime.

After dissociation of one of the tethers, the remaining single tether will carry the full load, until its adhesin dissociates. We calculated this case in Eqn S16, thus $\langle\tau\rangle_{C_3}$ is $\frac{1}{r_A(f)}$. Combining these events, we get the lifetime of coordinated failure $\langle\tau\rangle_C$

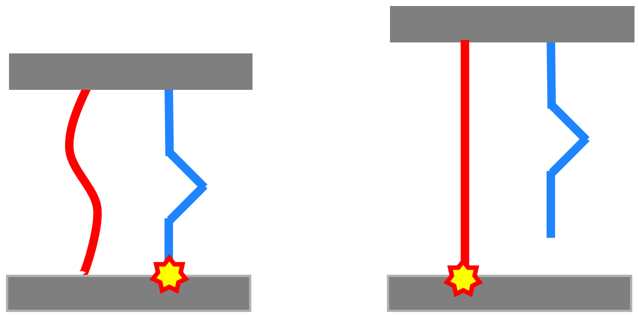
$$\langle\tau\rangle_C = \langle\tau\rangle_{C_1} + \langle\tau\rangle_{C_2} + \langle\tau\rangle_{C_3} = \frac{1}{r_A(f)+r_L(f)} + \frac{1}{2r_A(f/2)} + \frac{1}{r_A(f)}. \qquad \text{(S20)}$$

Lifetime of two-tether system

When we plug Eqn. S11, S17 and 20 into Eqn. S1, we get an analytical lifetime equation for the two-tether system:

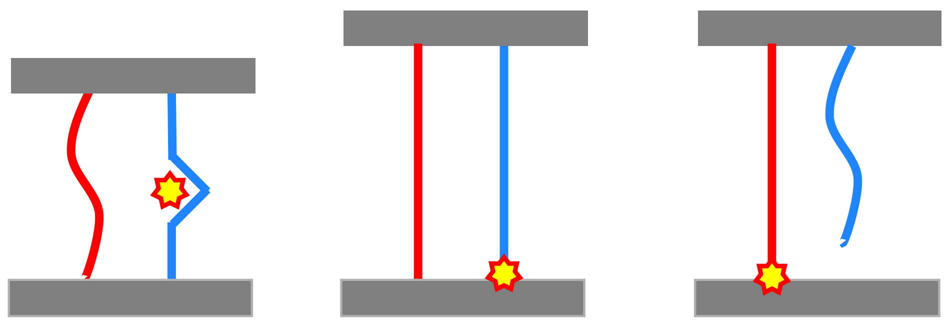
$$\langle\tau\rangle = \frac{r_A(f)}{r_A(f)+r_L(f)}\left(\frac{1}{r_A(f)} + \frac{1}{r_A(f)+r_L(f)}\right) + \frac{r_L(f)}{r_A(f)+r_L(f)}\left(\frac{1}{r_A(f)+r_L(f)} + \frac{1}{2r_A(f/2)} + \frac{1}{r_A(f)}\right). \qquad \text{(S21)}$$

Sequential failure



$$\langle\tau\rangle_S = \underbrace{\frac{1}{r_A(f)+r_L(f)}}_{\langle\tau\rangle_{S_1}} + \underbrace{\frac{1}{r_A(f)}}_{\langle\tau\rangle_{S_2}}$$

Coordinated failure



$$\langle\tau\rangle_C = \underbrace{\frac{1}{r_A(f)+r_L(f)}}_{\langle\tau\rangle_{C_1}} + \underbrace{\frac{1}{2r_A(f/2)}}_{\langle\tau\rangle_{C_2}} + \underbrace{\frac{1}{r_A(f)}}_{\langle\tau\rangle_{C_3}}$$

Fig. S1 Schematics of sequential and coordinated failure scenarios. In sequential failure, S_1 and S_2 mark adhesin dissociations. In coordinated failure, C_1 marks the unfolding of the loop, C_2 and C_3 mark adhesin dissociations. The lifetimes of these events are denoted with $\langle\tau\rangle$.

Effects of rebinding on the lifetime curve

In MD simulations, bond breaking and rebinding events are allowed to occur. To single out the effects of the rebinding on lifetime curves, we ran MD simulations where the rebinding is allowed. For these simulations, we imposed a distance criterion for the adhesion interaction with the bottom plates. When the distance between an adhesin and the bottom plate particle that adhesin interacts with, exceeds 2.36 Å (a bond rupture event), we changed the particle type of the adhesin to nullify this interaction and effectively disallow rebinding. The value of 2.36 Å corresponds to -0.001 kcal/mol adhesion energy in the energy landscape of the adhesive (E_A), which is small enough to consider the bond ruptured. In Figure S2, we show that rebinding actually increases the gain of the catch bond, and with no rebinding the catch bond effect is slightly diminished. From this, we conclude that rather than masking the catch bond behavior, rebinding seems to promote the catch bond behavior in our MD simulations, resulting in a slight increase in gain.

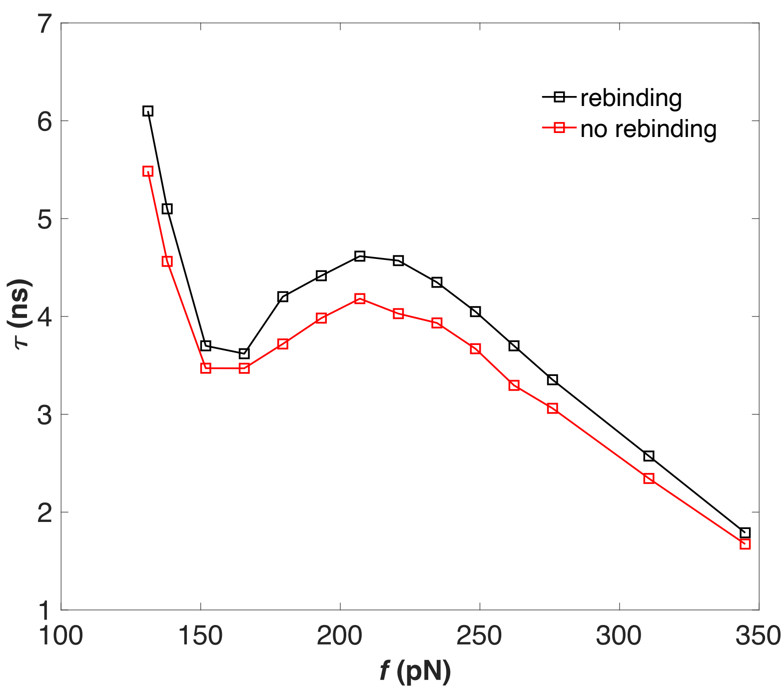


Fig. S2 Effects of rebinding on the lifetime curve

Codes:

All simulation input scripts and codes can be found at the following repository:

https://github.com/keten-group/2tethermodel