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Force-dependent bond dissociation explains the rate-dependent fracture of vitrimers†

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We investigate the rate-dependent fracture of vitrimers by conducting a tear test. Based on the relationship between the fracture energy and the thickness of vitrimer films, we, for the first time, obtain the intrinsic fracture energy and bulk dissipation of vitrimers during crack extension. The intrinsic fracture energy strongly depends on tear speed, and such dependence can be well explained by Eyring theory. In contrast, the bulk dissipation only weakly depends on tear speed, which is drastically different from observations on traditional viscoelastic polymers. We ascribe such a weak rate-dependence to the strong force-sensitivity of the exchange reaction of the dynamic covalent bond in the vitrimer.

1 Introduction

Vitrimers have recently emerged as a promising class of polymer for a variety of potential applications[1]. Due to the presence of associative exchange reactions in the polymer network, vitrimers combine desired features of both thermosets and thermoplastics, such as stable high-temperature properties together with distinct reprocessability. Although intensive research has been conducted for understanding the constitutive properties of these new materials, their fracture behaviors have been largely unexplored.

Continuous exchange reactions of dynamic covalent bonds make vitrimers "strong" viscoelastic materials[2,3], namely, the dependence of their viscosity on temperature can be described by Arrhenius law. Despite intense efforts made in the past, quantitative modeling or prediction of fracture in viscoelastic polymers remains challenging[4]. The difficulties are mainly two-fold: first, the molecular origin of the fracture process, together with its dependence on rate is still unclear; this not only blurs the interpretation of experimental results but also hinders the rational design of tough polymers[5]; second, during crack propagation, bulk dissipation often competes with the crack propagation process in a complex and rate- dependent manner[6]. To tackle the first challenge, either simple theoretical models such as the Lake-Thomas theory or empirical cohesive laws have been adopted[5]. The issue with these models however, is that they are usually based on the assumption that the intrinsic fracture energy or the cohesive law is rate independent. To overcome the second difficulty, a linear rheology model is often adopted for viscoelastic polymers when modeling its fracture[4,7–11]. As a result, the bulk dissipation in the material caused by crack propagation is often quite rate-sensitive[4,10]. However, those simplifications are often not sufficient to accurately capture the complex fracture phenomenon observed in viscoelastic polymers[12].

2 Results

In this article, we aim to reveal critical insights into the fracture process of viscoelastic vitrimers through a combined experimental study and theoretical analysis. For this, we first conduct tear experiments on thin vitrimer films. By varying the thickness of the film, we can experimentally measure the dissipated energy in the fracture process zone (also known as intrinsic fracture energy) as well as the bulk dissipation in the film accompanied with crack extension (Fig. 1). We find that the intrinsic fracture energy is highly rate-dependent, which is in contrast with the (rate-independent) assumption adopted in most previous studies on the fracture of viscoelastic polymers[4,10]. Using concepts from the classical Eyring theory, we are then able to successfully explain the scaling relationship between the vitrimer's intrinsic fracture energy and the tearing speed. This study also reveals that the bulk dissipation in the vitrimer film is only weakly dependent on the tearing rate within a range that spans three orders of magnitude; this finding is in contrast to previous studies on conventional viscoelastic polymers and gels[13,14]. We ascribe such weak

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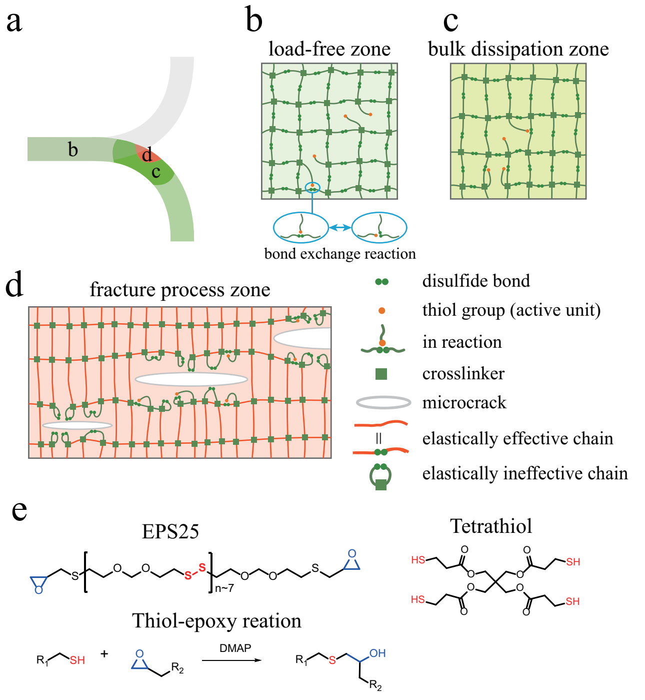

Fig. 1 (a) Fracture process zone and bulk dissipation zone in the vitrimer in one of two arms of the specimen during the tearing test from side view. (b) Associative exchange reactions (thiol-disulfide exchange reactions in Fig. S1) can happen in load-free zone. The thiol group is from the crosslinking molecules. (c) Associative bond exchange reactions occur more frequently in the bulk dissipation zone. (d) We assume that the formation of microcracks in fracture process zone reduces the areal density of elastically effective crosslinks (Σ_b) and increases the density of elastically ineffective crosslinks. (e) Chemical structures of the monomer (EPS25) and the crosslinker (tetrathiol) for synthesizing the vitrimer in this study; crosslinking is achieved through thiol-epoxy reaction with DMAP (4-Dimethylaminopyridine) as the catalyst.

rate-dependence of the bulk dissipation to the strong force sensitivity of the dynamic exchange reaction. Taken together, our study provides the first demonstration that thin-film tear test can be used to reveal critical insights into the fracture behavior of vitrimers.

Fig. 2(a) shows the schematic of the tear test adopted in our study, where a vitrimer film, glued to an inextensible backing layer, is introduced with a cut along its center line. More details of the material can be found in Supplementary and Ref. 15,16. In the test, one arm is fixed, and the other arm is stretched at a speed of v_0 as shown in Fig. 2(a). Since the backing layers constrain the sample deformation and the geometrical symmetry, the crack extension speed v is $\frac{1}{2}v_0$. Compared to many other fracture tests such as pure shear, single-edge notched tension, compact tension and center cracked tension, the tear tests adopted in our experiment, similar to the peeling tests for measuring adhesion, have two advantages. First, the crack propagation speed can be easily controlled by the pulling speed. Second, by changing the sample thickness, the intrinsic fracture energy and the bulk dissipation can be simultaneously measured based on a simple scaling law without needing specific material models[17,18].

In the experiments, we measure the force-extension relation of thin vitrimer films with different thicknesses (h=1 mm, 1.5 mm, 2 mm and 2.5 mm) and different tearing speeds (v_0/h=0.01/s, 0.1/s, 1/s and 10/s) as shown in Fig. 3 and Fig. S2. To analyze our experimental results, we normalize the crack velocity by introducing the normalized crack velocity $\overline{V} = (v_0\tau)/h$, where τ=42 s is the characteristic relaxation time of the vitrimer determined by its stress relaxation measurement at a small strain (5%) as shown in Fig. S3(a), and h is the film thickness as shown in Fig. 2(a). We also conducted shear creep [τ=44 s, Fig. S3(b)] and small-amplitude oscillation shear [τ=40 s, Fig. S3(c)] experiments on Rheometer to measure the characteristic relaxation time of vitrimers, which is obtained by fitting a Maxwell model to the measurements. It is noted that the characteristic relaxation time of the vitrimer is obtained from the three independent experiments are all comparable. In the experiment, the normalized crack velocity ($\overline{V}$) is varied between 0.42 to 420. When $\overline{V}$ is larger than 1, the crack surface is smooth as shown in Fig. 2(b), indicating quasi-brittle fracture. In each experiment, the pulling force oscillates around a plateau value (F) after an initial increase [Fig. 3], indicating a stick-slip crack growth[18]. Here we do not study the stick-slip dynamics, and simply use the average tear force on plateau F (obtained by averaging the measured force between the displacement of 30 mm and 90 mm) to estimate the energy release rate G. Because of the simple geometry and the inextensible backing layer, the energy release rate can be given by $G = 2F/h$.[18]

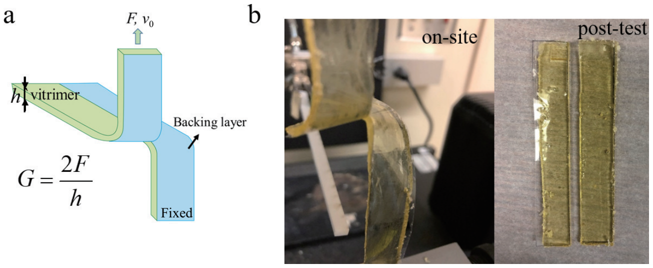

Fig. 2 (a) A schematic of tear test: one arm is fixed, and the other arm is stretched at a speed of v_0. (b) Tearing the vitrimer and the torn vitrimer with a smooth crack surface.

In Fig. 4, we plot the energy release rate G as a function of the film thickness h for four different crack velocities $\overline{V}$. We find that the relationship between the energy release rate and the film thickness is linear for all of the four different crack velocities ($\overline{V}$). Such linear relationship indicates that the size of the fracture process zone or "fractocohesive length" (R_0) is much smaller than the film thickness[17,18], as shown in Fig. 1(a), so we can separate the fracture energy into two parts:

$$G = G_c + G_d, \tag{1}$$

where G_c is the energy dissipation (intrinsic fracture energy) in the fracture process zone [Fig. 1(d)], and G_d is the energy dissipated by viscoelastic loss in the bulk of the film [Fig. 1(c)].

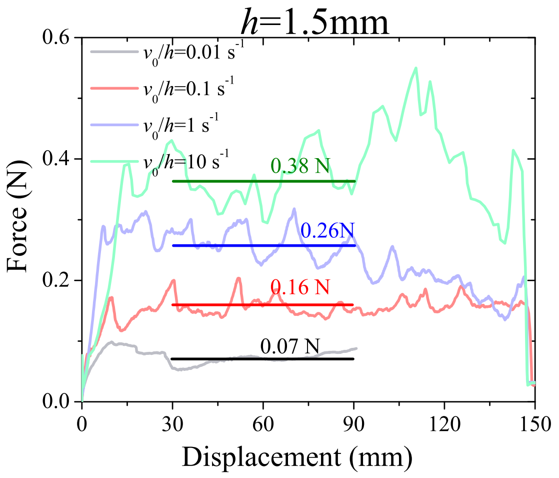

Fig. 3 Force vs. Displacement of tear experiments with the film thickness of 1.5 mm.

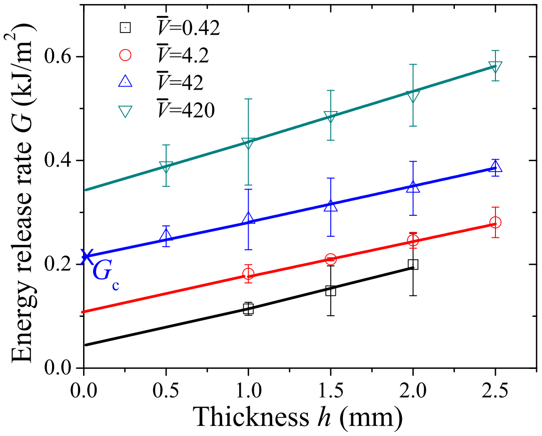

Fig. 4 Energy release rate as a function of thickness of the films with different normalized crack velocities $\overline{V}$.

3 Discussion

Based on de Gennes's model for fracture in a viscoelastic material[10,19], the size of bulk dissipation zone in the material is given by $R_d = \frac{E_0}{E_\infty} R_0$, where E_0 is the instant modulus, and E_∞ is the equilibrium modulus. For a vitrimer, the equilibrium modulus is zero, so the characteristic size of bulk dissipation in a vitrimer is infinitely large. As a result, the film thickness h is the only relevant length scale for bulk dissipation and thus $G_d \propto h$.[17,19] Our experimental data in Fig. 4 also suggests the linear dependency of G_d on h, so $G = G_c + w_p h$, where G_c is independent of h and w_p is the average density of bulk dissipation[20]. Based on this equation, the intersection of the fitted linear relationship between G and h with the vertical axis gives the intrinsic fracture energy G_c, as shown in Fig. 4. By measuring the slopes of the fitting lines relating the energy release rate G and the thickness h in Fig. 4, we can further measure the magnitude of w_p .

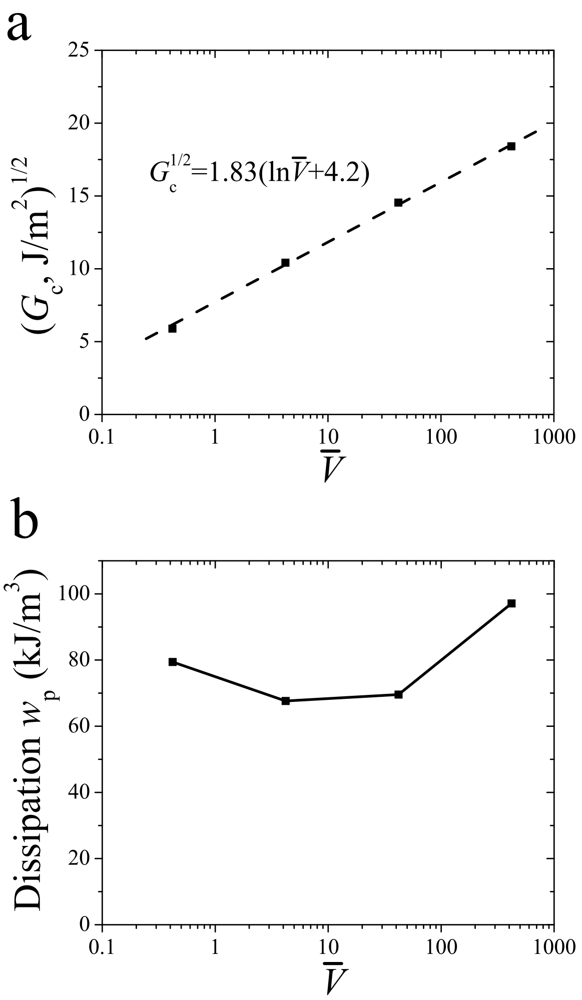

Fig. 5 (a) The intrinsic fracture energy as a function of the normalized crack velocity, where the intrinsic fracture energies are the interceptions of the lines with vertical axis in Fig. 4; (b) Bulk dissipation of vitrimer with different normalized crack velocities, where bulk dissipation is the slopes of the lines in Fig. 4.

We envision different energy dissipation processes in the area near the crack tip and in the bulk. In the bulk, the energy dissipation is mainly through viscoelasticity resulted from dynamic exchange reactions. However, moving towards the crack tip, the chains are increasingly stretched due to the stress concentration. According to the work of Chaudhury[21], this leads to an increase in the bond exchanging rate. The accelerated bond exchanging rate can facilitate the formation of cavities or microcracks. With associative bond exchange, though the crosslink density remains unchanged in the vitrimer, the elastically effective chains may become elastically ineffective (such as loops as shown in Fig. 1d). Therefore, within a small region near the crack tip, the network loses its integrity as irreversible damage occurs.

Fig. 5(a) plots the intrinsic fracture energy G_c as a function of the normalized crack velocity ($\overline{V}$). The strong rate-dependent intrinsic fracture energy of our vitrimer is in contrast to the assumption of rate-independent intrinsic fracture energy of viscoelastic polymers commonly adopted in previous studies[4,10,13]. It is also noted that the magnitude of G_c is much larger than the value ($21.2\ J/m^2$) predicted from the Lake-Thomas model (see the supplementary information).[20] As shown in Fig. 1, we believe that a fracture process zone, which is much larger than the mesh size of the polymer network, exists near the crack tip during tearing. To explain the scaling relationship between G_c and the crack velocity ($\overline{V}$), we extend the theory developed by Chaudhury and Hui[21,22] and assume that in the fracture process zone, the energy dissipation is mainly caused by accelerated bond dissociation. Similar to the picture depicted by Lake and Thomas[23], the energy stored (denoted as W) in a polymer chain is entirely dissipated and we have $G_c \sim \Sigma W$, where Σ is areal density of polymer chains.

According to Eyring theory, the force f applied to a chain modifies the energy landscape for bond dynamics. This leads to an increase in bond exchange rate $k_d = \tau^{-1}\exp(\frac{f\Delta_a}{k_BT})$, where τ is the natural frequency for bond exchange[24]. In the fracture process zone, we assume that polymer chains that experience exchange reaction become elastically ineffective and lose their load-bearing capacity [Fig. 1(d)]. Consequently, the decrease in the areal density Σ_b of elastically effective crosslinks follows the rate equation:

$$-\frac{D\Sigma_b}{Dt} = \tau^{-1}\exp\left(\frac{f\Delta_a}{k_BT}\right)\Sigma_b, \tag{2}$$

where k_B is the Boltzmann constant, Δ_a is the activation length of the covalent bond, and T is the absolute temperature. The frequency of bond exchange follows the Arrhenius law, $\tau = k_0\exp(\frac{E_a}{k_BT})$, in which k_0 is precursor and E_a is the activation energy of bond exchange without external force. Considering linear chains with spring stiffness k_s, the force is related to deformation as $f = k_s\delta = k_s\varepsilon_{chain}L_0$, where δ, ε_{chain}, and $L_0 = \sqrt{n}l$ are respectively the extension, strain and end-to-end distance of the polymer chain in a free standing state with n and l the number and length of Kuhn segments in a chain, respectively.

The force-sensitivity of bonds described in Eq. (2) can be experimentally explored by subjecting the vitrimer to a stress relaxation test. Indeed, during the relaxation process, once a polymer chain dissociates at fixed strain it no longer contributes to the network mechanics since free chains reassociate in a stress-free state, and the term of chain reassociation in Eq. (2) does not contribute to the stress. Therefore, the characteristic relaxation time of the network when a force f is applied on a polymer chain in Eq. (2) is $\tau_R = \tau\exp(-\frac{f\Delta_a}{k_BT})$. With the linear spring assumption of the polymer chain, we find that:

$$\ln(\frac{\tau_R}{\tau}) = -\Psi\varepsilon_{chain} \tag{3}$$

with the force sensitivity of bonds $\Psi = \frac{k_s\Delta_aL_0}{k_BT}$. This implies that the force sensitivity (Ψ) of the bond is a material parameter that remains constant during stress relaxation. The experimental results of the relaxation of vitrimer at different strains are shown in Fig. 6(a). We find that the stress reduction follows an exponential decay as: $\sigma/\sigma_0 = \exp(-t/\tau_R)$. To extract the force sensitivity of dynamic covalent bond, we employ the eight-chain model[25] and extract the strain of the polymer chain as $\varepsilon_{chain} = \sqrt{I_1/3} - 1$, where I_1 is the first invariant of the left Cauchy-Green deformation tensor and $I_1 = (1+\varepsilon)^2 + 2/(1+\varepsilon)$ for uniaxial tension with ε the tensile strain. Fig. 6(b) shows the experimental result of relaxation time as a function of the strain, where a linear relationship between $\ln(\frac{\tau_R}{\tau})$ and ε_{chain} is found and can be fitted by Eq. (3). The slope of line can be used to extract the force-sensitivity of dynamic disulfide bonds as $\Psi = 58.44$. This force sensitivity can be also estimated as follows. The spring stiffness of a polymer chain can be estimated by the modulus of the elastomer E and the mesh size of the network L_0 as $k_s \sim EL_0$, where $E \sim 1MPa$ is Young's modulus[15] and $L_0 \sim 10nm$ (see supplementary information) of our vitrimer. So, the spring stiffness of polymer chain k_s is in an order of 0.01 N/m. With the consideration of the activation length of disulfide bonds $\Delta_a \sim 0.3nm$ and temperature $T \sim 300K$, we can estimate the force sensitivity is $\Psi = (k_s\Delta_aL_0)/(k_BT) \sim 10$, which has the same order of the value of force sensitivity measured from stress relaxation in Fig. 6(b).

We next investigate the role of the bond's force sensitivity on the rate-dependent intrinsic fracture energy measured in the experiment [Fig. 5(a)]. If we assume that the rate of bond reassociation is negligible in the fracture process zone, Eq. (2) can be rewritten as

$$v_c\frac{D\Sigma_b}{D\delta} = -\frac{1}{\tau}\Sigma_b\exp\left(\frac{f\Delta_a}{k_BT}\right), \tag{4}$$

where the velocity of chain stretch is $v_c = d\delta/dt$. v_c can be estimated from the crack velocity as follows: due to the existence of a backing layer, the material deformation is constrained into a small region of length h around the moving crack tip[18]. Therefore, a characteristic time for chain deformation is obtained as $t_0 = h/v_0$. Furthermore, since the surface is fully separated at the end of the deformation zone, we assume that chains are elongated from their natural length $\sqrt{n}l$ to the contour length nl when they travel through the deformation zone. Based on this conceptual picture, the chain's stretch rate can be estimated as $v_c = (\sqrt{n}-1)L_0v_0/h$ in Eq. (4). An average dissociation length of polymer chain can be defined as $\overline{\delta} = \int_0^\infty \frac{\Sigma_b}{\Sigma_0}d\delta$. By recalling Eq. (4) and following the derivation of Chaudhury[21], the integration can be obtained as $\overline{\delta} = \frac{k_BT}{k_s\Delta_a}\ln\left[\Psi(\sqrt{n}-1)\overline{V}\right]$, if $k_s\Delta_aL_0\overline{V} \gg k_BT$[22,26]. The average force on a chain before failure can be expressed as $f_{break} = k_s\overline{\delta}$ and the average energy stored in a polymer chain before breakage is $W = \frac{1}{2}k_s\overline{\delta}^2$. Invoking our scaling analysis, the intrinsic fracture energy G_c therefore scales as:

$$G_c \propto \{\ln\left[\Psi(\sqrt{n}-1)\overline{V}\right]\}^2 \tag{5}$$

or $\sqrt{G_c} = \alpha(\ln\overline{V} + \beta)$, where the coefficient α is related to the thermally activated force-sensitivity of dynamic covalent bonds and the size of the fracture process zone, while the coefficient β is a rate-independent constant expressed as

$$\beta = \ln\left[\Psi(\sqrt{n}-1)\right]. \tag{6}$$

From Eq. (5), we know that $\sqrt{G_c} \propto \ln\overline{V}$, which agrees well with the result shown in Fig. 5(a). A good agreement between model and experiment is further obtained with $\beta = 4.2$ by the fitting shown in Fig. 5(a).

As shown in Fig. 6, we can also evaluate the coefficient β defined in Eq. (6), based on that $\Psi = 58.44$, determined from the stress relaxation measurements previously, and the number of

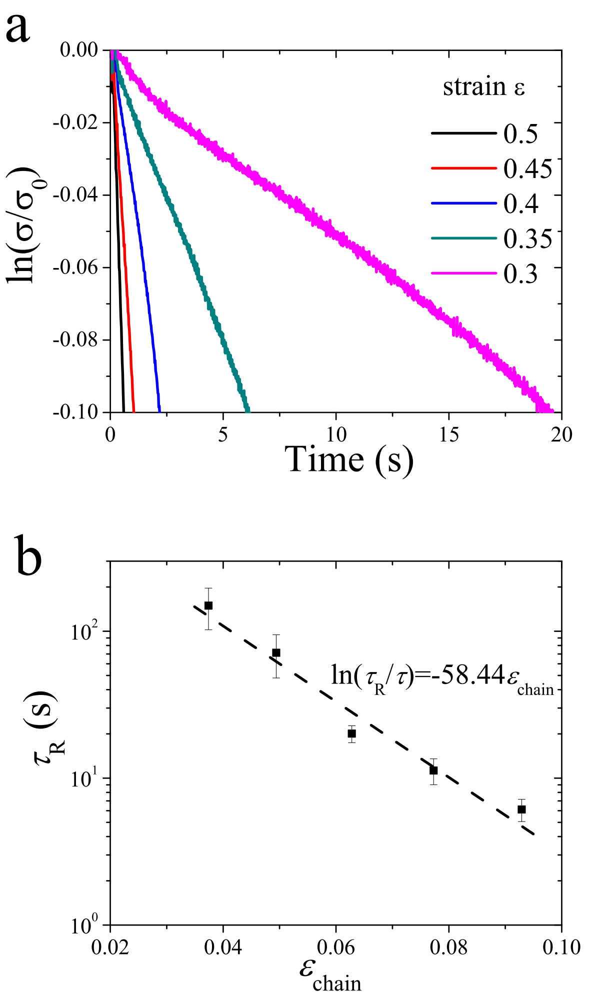

Fig. 6 (a) Stress relaxation of a vitrimer with different applied strains ε. (b) Relaxation time as a function of the chain strain ε_{chain}.

Kuhn segments n. To estimate the number of Kuhn segments of the vitrimer for our experiment, we conducted uniaxial tension tests on a thin vitrimer strip with a strain rate of 100%/s. For such a strain rate, the bond exchange reaction is negligible during the deformation. We found that the rupture strain of the vitrimer strip is around 150% as shown in Fig. S4. According to the eight-chain model[25], the chain locking stretch (defined as the stretch of a chain when it is fully extended) can be estimated from the rupture strain of the vitrimer strip as $\lambda_L = 1.54$, under the assumption that the polymer chain is fully extended at rupture. The number (n) of Kuhn segments could further be related to the chain locking stretch (λ_L) as $\lambda_L = \sqrt{n}$, which yields $n = 2.4$. Consequently, we can obtain $\beta = 3.5$, which is close to the one estimated from the measurement of the rate-sensitivity of the intrinsic fracture energy shown in Fig. 5(a).

Another notable result of this study pertains to the rate of bulk dissipation w_p. Indeed, Fig. 5(b) suggests that w_p is only weakly dependent of the tearing rate, varying between $65 \sim 98 kJ/m^3$ over the range of $\overline{V}$ from 0.42 to 420. This weak rate-dependence is in sharp contrast to the rate-dependent bulk dissipation of most viscoelastic polymers studied in the past[13]. For a linear viscoelastic material, it is expected that bulk dissipation should reach a maximum when the loading time is comparable to the single relaxation time of the material, and reach a minimum when the loading rate is too small or too large, as shown in Fig. S5(a-b). We postulate that such difference is caused by the nonlinear viscoelasticity of the vitrimer, where the rate of bond exchange increases at larger forces or strains and thus there is no single relaxation time in the material. The stretch-stress curve of a strongly force-sensitive vitrimer (using $\Psi = 58.44$) experiencing loading-unloading history at different loading rates, is calculated by combining the classic transient network theory with Eyring's theory and steady-state kinetics for chain dissociation and reassociation[6], as shown in Fig. S5(c). The strong force-sensitivity of dynamic covalent bonds leads to large bulk dissipation even when $\overline{V}$ is very large e.g. $\overline{V} = 42,420$, as shown in Fig. S5(d). A more detailed study of w_p in the tear test of a vitrimer film requires a full-field simulation of the tearing process with a nonlinear viscoelastic material model, which is a challenging task and has not been achieved in the literature yet. However, in this work, we circumvent this difficulty and simply extract the effect of w_p on the fracture energy based on geometric scaling.

4 Conclusions

In summary, our study clearly shows that tear test of a vitrimer film is an effective way to explicitly reveal the molecular origins of rate-dependent energy dissipation associated with its fracture. Through the experiment, we find that the intrinsic fracture energy of vitrimers with disulfide bonds is highly rate-dependent while their bulk dissipation is rather rate-insensitive during fracture; this is in significant contrast with most previously studied viscoelastic polymers. By assuming a small fracture process zone near the crack tip within which the acceleration of bond dissociation is the main energy dissipation mechanism, we could explain the scaling relationship between the intrinsic fracture energy and the normalized crack velocity based on the classical Eyring theory.

Conflicts of interest

There are no conflicts to declare.

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