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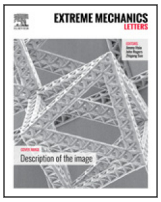

Hydrolytic crack in a rubbery network

Xuxu Yang [a,b,1], Jiawei Yang [a,1], Liyuan Chen [a,b], Zhigang Suo [a,*]

[a] John A. Paulson School of Engineering and Applied Sciences, Kavli Institute for Bionano Science and Technology, Harvard University, Cambridge, MA, 02138, USA
[b] Department of Engineering Mechanics, Zhejiang University, Hangzhou, Zhejiang, 310027, PR China

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ABSTRACT

We report an experimental finding that a crack advances in a polydimethylsiloxane (PDMS), under a small stress, in a moist environment. PDMS chains consist of siloxane bonds with methyl side groups. The methyl groups make PDMS hydrophobic, and PDMS hydrolyzes extremely slowly under no stress. Nonetheless, we find that a crack advances under the combined attack of water and stress. Our experimental data support the hypothesis that PDMS is susceptible to stress-assisted hydrolysis, but show that the activation area for PDMS is smaller than that for silica by two orders of magnitude. We attribute this large difference to the molecular structures of the two materials: a glassy network and a rubbery network, respectively. This finding suggests that stress-assisted reaction should concern many elastomers and gels in engineering and medicine.

Silica can sustain a small stress in a moist environment for some time before rupture. Since its discovery over a century ago [1], this delayed fracture has been studied extensively, and its practical importance has grown enormously as silica finds applications beyond glassware and windows, such as composites, optical fibers, and screens [2–5]. The delayed fracture results from stress-assisted hydrolysis [6,7] (Fig. 1a). The surface of silica inevitably has crack-like flaws. Even when the silica carries a small stress, the sharp tip of a crack concentrates stress. The strained siloxane bonds at the crack tip react with water molecules in the environment to form silanol groups, $\text{Si–O–Si} + H_2O \rightarrow 2\text{Si–OH}$, advancing the crack. When the crack reaches a critical size, the silica ruptures. The rate of stress-assisted hydrolysis is commonly characterized by measuring the velocity of a crack as a function of humidity and mechanical load [8–10].

We hypothesize that stress-assisted hydrolysis also advances cracks in many elastomers, even when the elastomers are hydrophobic. We test this hypothesis using polydimethylsiloxane (PDMS) (Fig. 1b). A PDMS polymer chain consists siloxane bonds with methyl side groups. The methyl groups make PDMS hydrophobic. Under no stress, PDMS hydrolyzes extremely slowly at room temperature. However, the methyl groups do not prevent the elastomer from cracking under the combined attack of water and stress, as our experiment will show. We make sheets of PDMS with precut cracks, stretch them in pure liquid water or in a humidity-controlled chamber, and measure the velocities of the cracks. Note that the hydrophobic methyl groups do not prevent water molecules from diffusing through the PDMS, and water molecules can fill up the crack tip of the PDMS. Our experimental data support the hypothesis that stress-assisted hydrolysis advances cracks in PDMS, but the activation area of PDMS is about two orders of magnitude smaller than that of silica. We interpret this result in terms of the different molecular structures of silica (a glassy network) and PDMS (a rubbery network).

We fabricate PDMS samples by mixing the base and curing agent (Dow Corning Sylgard 184) with a ratio of 20:1. The PDMS precursor is degassed, and cured in an acrylic mold (50 mm × 100 mm × 1.5 mm) for one day at the temperature of 65 °C. At a loading rate of 10 mm/min, the PDMS has a shear modulus of 0.12 MPa, stretchability of approximately 2, and toughness of 390.9 ± 10.8 J/m^2.

PDMS is transparent. To better visulize the crack, we coat the PDMS sample with a thin layer of dyed PDMS. We add a dye (Createx airbrush colors, 5211 Opaque Black) into another PDMS precursor of the same base/agent ratio, with the dye being half the weight of the curing agent, and spin coat a thin layer of the dyed PDMS of thickness about 10 µm (1500 rpm for 1 min) on the molded PDMS. The dye is uniformly dispersed and trapped in the thin PDMS layer, and does not diffuse into the molded PDMS.

We adopt a standard experimental setup in the fracture mechanics of elastomers (Fig. 2a) [11]. PDMS samples are clamped in two rigid fixtures, and the final dimension of tested PDMS sample is $L = 100$ mm, $B = 1.5$ mm, and $H = 20$ mm. A cut of $c = 40$ mm is subsequently made in the PDMS sample using a razor blade. The samples are pulled vertically, and held at a constant stretch λ subsequently. At the fixed displacement, the reduction

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[*] Corresponding author.
E-mail address: suo@seas.harvard.edu (Z. Suo).
[1] These authors contributed equally to this work.

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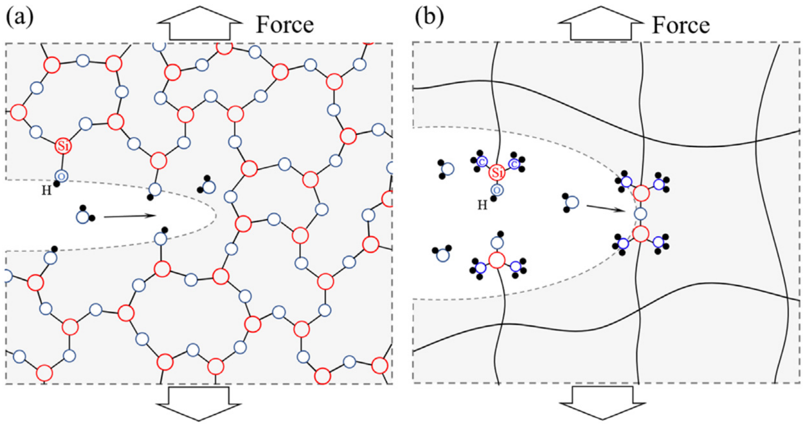

Fig. 1. Stress-assisted hydrolysis. When a siloxane-bonded material is subject to a tensile force, the tip of a crack concentrates stress, which assists hydrolysis. The reaction converts siloxane bonds to silanol groups, advancing the crack. (a) Silica (SiO_2) is a glassy network that contains siloxane bonds. (b) Polydimethylsiloxane (PDMS) is rubbery network that contains siloxane bonds.

of the elastic energy associated with the advance of the crack by a unit area defines the energy release rate, $G = HW(\lambda)$, where H is the height of the sample in the undeformed state, and $W(\lambda)$ is the work per unit volume measured using a PDMS sample of same dimension but without precut crack (Fig. 2b). The energy release rate for fast crack growth defines the toughness. When we immerse a PDMS with a precut crack in pure liquid water without applying stretch, the crack does not advance based on our observation.

We first study the effect of humidity on crack growth. We immerse a PDMS sample in pure liquid water, and apply a fixed energy release rate of 60 J/m^2. The applied energy release rate is smaller than the toughness of PDMS, so that the crack does not extend rapidly, but does extend slowly (Fig. 3a). The crack length is recorded by a digital camera (resolution ∼0.1 mm). We also subject a PDMS sample under the same energy release rate, but in a chamber of a relative humidity RH = 11.3%, where the crack also extends, but at a much lower velocity than in pure liquid water (Fig. 3b). The length of the crack grows linearly as a function of time, indicating a steady growth (Fig. 3c). The crack velocity is on the order of 10^{-6} m/s for the sample tested in pure liquid water, and 10^{-8} m/s for the sample tested at RH = 11.3%.

We further measure crack velocities in the chamber of a range of relative humidity from 5% to 95.5% (Fig. 3d). The relative humidity is controlled using either desiccants or saturated salt solutions, which are stored in a sealed chamber in advance for several hours to allow the relative humidity reaching equilibrium [12] (Calcium oxide: RH = 5%; Lithium chloride: RH = 13.3%; Magnesium chloride: RH = 33.1%; Magnesium nitrate: RH = 54.4%; Sodium chloride: RH = 75.5%; Potassium nitrate: RH = 95.5%). PDMS samples are then placed in the chamber. The PDMS samples contact with the ambient vapor directly, but not the desiccants and the salt solutions.

We next study the effect of energy release rate on crack growth. All tests are conducted in pure liquid water, and the energy release rate is varied by applying different stretches to the PDMS samples. The crack velocity decreases as the energy release rate reduces (Fig. 4). Also included for comparison is the experiment data of silica [10]. The two sets of data differ greatly.

We interpret these experimental findings in terms of the molecular structures of silica and PDMS. Silica is a glassy network (Fig. 1a). Even under a small stress, the siloxane bonds at a crack tip are highly strained, react with water molecules, and convert into silanol groups. The chemical reaction breaks only one layer of siloxane bonds and creates two surfaces covered with monolayers of silanol groups. All other siloxane bonds inside the network remain intact. This picture was due to Griffith [13], and has since modified to include hydrolysis [6]. After a siloxane bond breaks, the two silanol groups remain nearby, and possibly condense back into a siloxane bond. The hydrolysis and condensation may reach a state of equilibrium, which correspond to a threshold. When the applied load is above the threshold, the chemical reaction goes forward, the siloxane bonds hydrolyze, and the crack advances. When the applied load is below the threshold, the chemical reaction reverses, the silanol groups condense, and the crack heals. Such a threshold, however, is not always observed in experiments on silica, and is in particular not observed in the data used in Fig. 4. The existence or absence of threshold depends on the detailed physical chemistry near the crack front [4].

PDMS is a rubbery network (Fig. 1b). Under a force, the polymer chains at a crack tip are stretched, and the siloxane bonds on the polymer chain react with water molecules. The chemical reaction breaks one layer of polymer chains, and creates two layers of dangling polymer chains with the silanol groups at their ends. This picture was due to Lake and Thomas [14], which we now modify to include hydrolysis. After a siloxane bond in the stretched polymer chain cleaves, the two silanol-ended polymer chains retract, and the two silanol groups may randomly bury inside coiled polymer chains and are difficult to find each other to condense back to a siloxane bond again. Therefore, the recombination of two broken polymer chains is unlikely. Consequently, the chemical reaction is irreversible, leading to non-equilibrium crack growth. Siloxane bonds hydrolyze, but silanol groups do not condense. The crack can only advance, but cannot heal. We do not expect any threshold. Next, we propose a kinetic theory of chain scission in a rubbery network.

Consider a polymer chain subject to a constant tensile force. Similar to the classic description of rate of bond cleavage [15], here, we neglect the term associated with the rate of bond condensation, and write the rate of chain scission as

$$\nu \exp\left(-\frac{E - fL^*}{kT}\right), \tag{1}$$

where ν is frequency of atomic vibration, E is the energy barrier for bond cleavage, f is the tensile force applied to the polymer chain, L^* is the activation length, and kT is the temperature in the unit of energy. The tensile force f changes the energy landscape of the chemical reaction, lowers the energy barrier from E to E-fL^*. Here, fL^* is the first-order term in the Taylor expansion of the energy barrier as a function of the force. Eq. (1) has long been used in analyzing cell adhesion [16], as well as in bond breaking

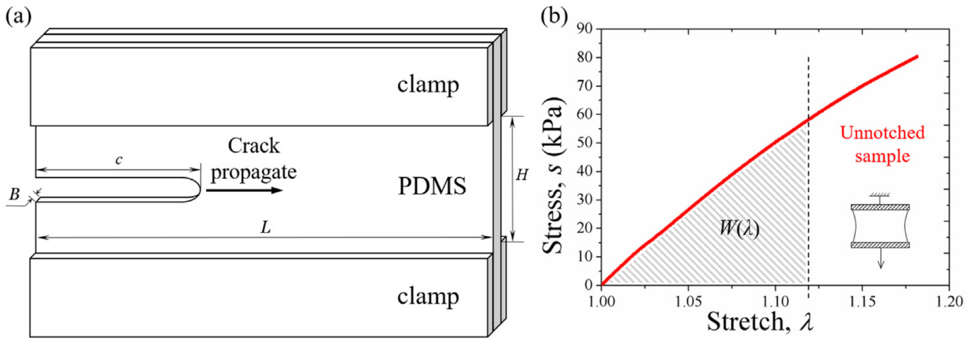

Fig. 2. Experiment setup. (a) A PDMS sample with a precut crack. (b) An unnotched PDMS sample is used to measure the stress–stretch curve. The stress s is defined by the applied force divided by the undeformed area, LB. The stretch λ is defined by the height of the deformed sample divided by the height of the undeformed sample. The area under the stress–stretch curve, $W(\lambda)$, is the work done by the applied force divided by the volume of the sample, LBH.

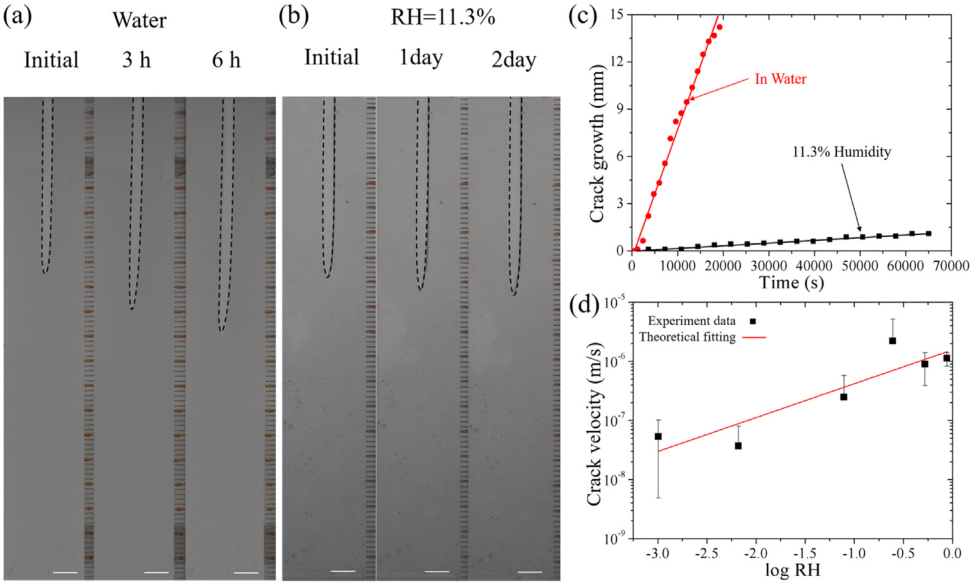

Fig. 3. Slow-growing crack in PDMS under the combined attack of stress and water. PDMS is stretched at an energy release rate of 60 J/m^2. A crack extends (a) in pure liquid water, and (b) at RH = 11.3%. The dashed line delineates the boundary of the crack. The scale bar is 5 mm. (c) The crack extends linearly in time. The crack velocity in pure liquid water is two orders of magnitude higher than that at RH = 11.3%. (d) Crack velocity as a function of relative humidity. Each data point represents 3–4 experiment results.

in single-molecule tests [17,18], such as covalent bonds [19], protein folding [20,21], DNA base-pair interactions [22], and mussel adhesion [23].

Next, we consider a polymer network with a crack and subject to an external force. The external force is not applied directly to individual polymer chain, but through the rubbery network. We modify Eq. (1) in term of the velocity of the crack and use the energy release rate as a load parameter

$$v \sim av \exp\left(-\frac{E - GA^*}{kT}\right), \tag{2}$$

where a is the extension of the crack associated with the scission of a polymer chain, and A^* is the activation area. G changes the energy landscape of the chemical reaction, lowers the energy barrier from E to E-GA^*. Here, GA^* is the first-order term in the Taylor expansion of the energy barrier as a function of energy release rate.

Write

$$v = v_0 \exp\left(\frac{GA^*}{kT}\right). \tag{3}$$

We expect that

$$v_0 \sim av \exp\left(-\frac{E}{kT}\right). \tag{4}$$

The energy release rate G is dissipated through a unit area of a layer of polymer chain [14]. The thickness of a layer of polymer chain is estimated as $b\sqrt{n}$, where b is the size of a monomer unit, n is the average number of monomer unit per polymer chain. Let V be the volume per monomer unit. The energy available to each bond is $GV/b\sqrt{n}$. This consideration estimates the scale of the activation area:

$$A^* \sim \frac{V}{b\sqrt{n}}. \tag{5}$$

The activation area A^* decreases as the polymer chain length increases. This simple picture predicts that a rubbery network has a lower activation area than that in a solid by a factor of $\sqrt{n}$.

Eq. (3) is a straight line in a semi-log plot, $\log v = \log v_0 + GA^*/kT$, with $\log v_0$ being the intercept, and A^*/kT being the slope. Fitting this straight line to the experimental data (Fig. 4), we obtain that $v_0 = 1.31 \times 10^{-11}$ m/s for PDMS and 4.99×10^{-18} m/s for silica, and $A^* = 5.82 \times 10^{-22}$ m^2 for PDMS and 2.87×10^{-20} m^2 for silica.

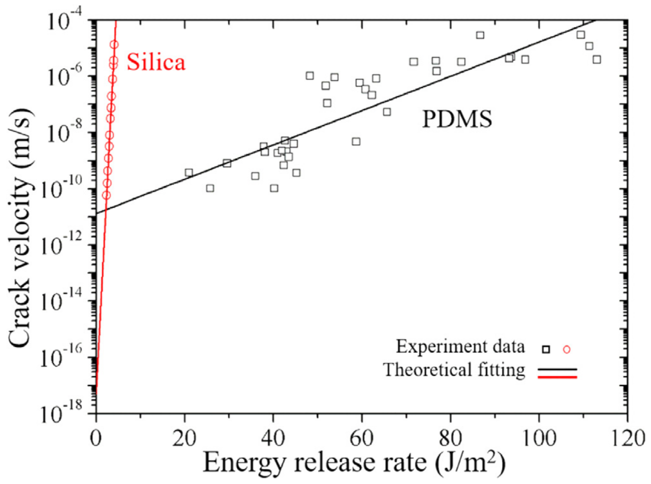

Fig. 4. Crack velocity as a function of energy release rate. Experiment data of PDMS (this work) and of silica [10] are both obtained from tests in pure liquid water. Each data point represents a single test.

Inspecting Eq. (4), since ν for the siloxane bond in silica and PDMS should be similar ($\nu \sim 10^{13}$ Hz), we expect that the large difference in v_0 arises from (i) the difference in the extension of the crack associated with the cleavage of each bond, and (ii) the difference in the energy barrier for hydrolysis. The crack extension in silica is atomic length, which is estimated as $a_{silica} = (A_\rho/M)^{-1/3} = 3.35 \times 10^{-10}$ m, where M is the molar mass of silica (60.08 g/mol), ρ is the density of silica (2.65 g/cm^3), and A is the Avogadro number (6.022×10^{23}). By contrast, the crack extension in PDMS is molecular length (i.e., the network mesh size), which is estimated as $a_{PDMS} = (S/kT)^{-1/3} = 3.25 \times 10^{-9}$ m, where S is the shear modulus of the PDMS (~0.12 MPa measured for PDMS in our experiment), and $kT = 4.11 \times 10^{-21}$ J at room temperature. Substitute above numbers into Eq. (4), and we obtain the energy barrier $E = 1.46 \times 10^{-19}$ J for PDMS and 2.03×10^{-19} J for silica. The difference may result from the chemical environment between dimethylsiloxane in PDMS and siloxane in silica. Both values are comparable to the dissociation energy of a siloxane bond in the presence of water ($\sim 2.36 \times 10^{-19}$ J) [24].

The activation area of PDMS is smaller than that of silica by two orders of magnitude. We interpret this large difference as follows. For PDMS (base/agent ratio = 20:1) we used, $n \sim 100$ [25]. The effect of chain length thus accounts for a difference about one order of magnitude. In arriving at Eq. (5), we have adopted the Lake-Thomas assumption that one layer of polymer chains dissipates energy during fracture. This assumption neglects other mechanisms of dissipation, such as the effect of fillers and distributed chain scission. These effects must exist in PDMS, because the toughness of PDMS is about 390 J/m^2 (measured in the work), whereas the toughness of silica is on the order of 1 J/m^2 [13]. This difference in toughness by two orders of magnitude suggests that PDMS must have dissipation mechanisms beyond the retraction of single layer of polymer chains. Mechanisms of dissipation in PDMS at various crack velocities are interesting topics by themselves, which are beyond the scope of this work.

Uncertainty about the mechanisms of dissipation aside, our experiments unambiguously show that crack velocity increase with the humidity (Fig. 3). This experimental finding supports the hypothesis that stress-assisted hydrolysis advances cracks in PDMS. We next incorporate the effect of humidity by writing

$$v = v_0 \exp\left(\frac{\mu N^* + GA^*}{kT}\right), \tag{6}$$

where μ is the chemical potential of water in the environment, and N^* is the activation number. μN^* is the first-order Taylor expansion of energy barrier as a function of chemical potential. We set the chemical potential of water to be zero in liquid water. Thus, the chemical potential of water in vapor is $\mu = kT\log(p/p_{st})$, where p is partial pressure of water vapor in the chamber, and p_{st} is the saturation pressure. The relative humidity is defined by RH $= p/p_{st}$, so that $\mu = kT\log(RH)$.

We use Eqs. (6) to fit experiment data in Fig. 3. The slope of the straight line gives the activation number $N^* = 1.35$. This value is somewhat larger than the typical value for silica, where $N^* = 0.5$ in the low humidity regime, and $N^* = 1$ in the high humidity regime [9]. This difference is probably due to a large crack tip opening in the PDMS, which allows water molecules to freely diffuse into the blunted crack tip for hydrolysis. A sufficient number of water molecules are available to attack the siloxane bonds, both in high and low humidity.

Early studies have showed combined stress and environmental species can degrade rubbery networks in terms of the loss of mass, the deterioration of mechanical properties, and the change of surface appearance. Examples include ozone attack in natural rubber [26], erosion of elastomers [27], and the pH attack in silicone rubber [28]. In ozone attack of natural rubber, degradation is observed in the absence of stress, and the presence of stress merely advances well-defined cracks [26]. In hydrolytic attack of PDMS, degradation may also occur in the absence of stress, but the rate of degradation is extremely slow, and the crack is not observed to advance in water in our experiment. The same crack, however, unambiguously advances under the combined attack of water and stress.

In summary, we show that cracks advance in PDMS under small stress in moist environment. We observe that the crack velocity in PDMS increases by orders of magnitude when the humidity and energy release rate increase. We develop a kinetic theory of chain scission in rubbery network and show that the activation area for PDMS is smaller than that for silica by two orders of magnitude. Other effects, such as crosslink density, temperature, pH, are of great interest and should be studied in future work. Our finding calls for action. Cracking by stress-assisted hydrolysis is expected in all polymers of hydrolyzable moieties, such as poly(lactide acid), polycaprolactone, and poly(lactic acid-co-glycolic acid) [29]. Furthermore, stress can assist other reactions, such as oxygen aging of elastomers [30], enzymatic degradation of proteins and polysaccharide [31,32], and chemical degradation of hydrogels [33]. The rich chemistry of polymers and environments offers an enormous space to study cracking in rubbery networks by stress-assisted reaction. The study is of immediate importance to existing and emerging applications in engineering and medicine, such as water matrix composites, ionotronics, bioelectronics, and medical implants.

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