



A poroelastic signature of the dry/wet state of a crack tip propagating steadily in a physical hydrogel

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ABSTRACT

We report detailed measurements of the rate-dependent fracture energy Γ of poroelastic gelatin gels for two distinct boundary conditions on the crack faces. When the crack tip is in contact with a reservoir of solvent, Γ increases linearly with the crack velocity V . When the tip is exposed to air, $\Gamma(V)$ exhibits a marked departure from linearity at low enough velocities. We show that viscous dissipation associated with poroelastic flow in the tip vicinity plays a minor role in this phenomenon. We interpret the previously overlooked, peculiar behavior of dry cracks as resulting from the rate-dependent hydration state of the gelatin chains in the cohesive zone, where they are pulled-out. At large velocities, the cohesive zone is fully dry and Γ is larger than in the wet tip case. At velocities low enough for solvent to flow from the bulk of the gel, partial rehydration occurs and reduces the difference between the dry and wet fracture energies.

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1. Introduction

Hydrogels, made of self-assembled biopolymer networks in aqueous solvents, are increasingly involved in load-bearing structures, such as implantable scaffolds for tissue engineering or patches for active wound dressings and drug delivery. In such applications, their interface with physiological fluids is clearly an issue since, with such highly stretchable materials, even subcritical surface flaws may widely open, their blunted tips being exposed to aggressive solutes. The extreme environmental sensitivity of crack growth in physical (non-covalently crosslinked) hydrogels has been revealed through several experimental studies [1–3]. It has been shown that water-soluble species can diffuse from the crack-tip opening into the process zone where they modify e.g. the solvent viscosity or the strength of the solvent/polymer interaction. Consequently, they can strongly affect (usually weaken) stationary or slowly propagating cracks.

The complex role of solvent flow on the mode I fracture toughness of a polymer gel containing a semi-infinite growing or stationary crack has recently motivated several theoretical and numerical studies [4–8] accounting for the poroelastic nature of the soft solids. It has been predicted that the fracture energy could be modified by (i) the time-dependent load transfer between the pore pressure and the network tension, and (ii) the rate-dependent viscous dissipation associated with solvent flow. Interestingly, the

poroelastic effect is found to depend on whether the sample, hence the crack tip, is in contact either with air or with a solvent bath. It has also been pointed out [7] that the existence of a finite size cohesive zone driving solvent flow in the near-tip region has profound consequences on the calculated toughness. The emerging picture is that of a rich and complex issue with lacking connections between experiments and theory.

In this paper, we revisit and extend previous experimental results on gelatin gels [1,9]. These physical networks are known to fracture without chain scission. Chains are entirely pulled-out in the cohesive zone and exposed either to air (*dry* crack) or to a drop of the gel solvent itself (*wet* crack). Extracting chains into air, rather than into their aqueous solvent, is known to induce an extra energy cost. We find that at low enough velocities, the corresponding excess of fracture energy for nominally dry cracks decreases and tends to vanish. We provide experimental evidence in favor of a simple picture where the cohesive zone of dry cracks is partially rehydrated by the poroelastic flow from the bulk of the sample, while for wet cracks, imbibition of the chains from the tip reservoir is complete, showing no measurable delay with respect to the crack advance.

We stress that detailed *macroscopic* measurements of the steady-state, rate-dependent fracture energy provide a reliable indicator of the state of rehydration of the *microscopic* cohesive zone in gelatin gels. The identification of a previously overlooked [1,9,10] low rate regime where dry cracks exhibit a peculiar behavior is the major outcome of this paper.

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2. A reminder on the fracture energy of single network, physical hydrogels

The low velocity (strongly subsonic) fracture dynamics in hydrogels for which physical, non-covalent crosslinks act as mechanical fuses preventing chain scission has been extensively described [1,9,10]. To a first approximation, the fracture energy $\Gamma(V)$ of a mode I crack steadily propagating at a velocity V in a gelatin gel is well described by a linear law: $\Gamma(V) = \Gamma_{wet}^{(0)} + \Delta\Gamma^{(0)} + \bar{\Gamma}\eta V$, where the shift factor $\Delta\Gamma^{(0)}$ is a constant, positive when the crack is “dry” i.e. in contact with air and null when the crack is “wet” i.e. in contact with a reservoir of the gel solvent. A cohesive zone model has been proposed to account for this expression. In brief, $\Gamma_{wet}^{(0)}$ corresponds to the energy paid for unzipping the extended crosslinks (triple helices in the gelatin case). The velocity-dependent term, featuring the solvent viscosity η , stems from the viscous dissipation cost of chain pull-out. $\bar{\Gamma}$ is a dimensionless geometrical factor. The shift $\Delta\Gamma^{(0)}$ was attributed [1] to the extra energy cost for exposing the extracted chains to air—a poor solvent for hydrophilic polymers. In this picture, owing to the scissionless rupture mechanism, the maximum crack-tip opening is the contour length $\Lambda \lesssim 1\mu\text{m}$ of the polymer chains which are stretched taut upon extraction. The depth d of the cohesive zone (Fig. 1) has been estimated experimentally [1] to be typically $d \simeq 100\text{ nm}$. It is important to emphasize that $d \ll \Lambda$, i.e. that the cohesive zone extends perpendicular to the crack plane. This behavior is characteristic of elastically blunted cracks [11] in soft solids for which the rupture stress is much larger than the elastic modulus, hence where *non-linear* elasticity is at work far beyond the cohesive zone [10,12,13].

3. Materials and methods

Gel samples are prepared as described previously [1,9] by dissolving gelatin powder (type A, from porcine skin, Sigma) in either a mixture containing $\phi = 60\text{ wt.}\%$ glycerol in deionized water or pure deionized water ($\phi = 0$), under continuous stirring at $60\text{ }^\circ\text{C}$ for 30 min. The hot pre-gel solution is then poured into a mold made of a rectangular metallic frame sandwiched between Mylar films covered by hard flat plates. The inner faces of the long sides of the frame are covered with Velcro tape which ensures good gripping of the gelled sample. The mold is then kept at $5\text{ }^\circ\text{C}$ during 15 h for gelation to proceed, before being clamped to the mechanical testing setup and left for 2 h at room temperature ($20 \pm 0.5\text{ }^\circ\text{C}$). The Mylar films are removed just before running the experiments to avoid solvent evaporation.

The resulting gel sample (length $L = 300\text{ mm}$, height $h = 30\text{ mm}$, thickness $e = 10\text{ mm}$) is first stretched by moving one of the gripping bars along the sample height direction up to $\Delta h_{\text{max}} = 8\text{ mm}$ at a rate of 12 mm s^{-1} , then immediately unloaded. The corresponding loading force $F(\Delta h)$ is measured by a stiff dynamometer made of a double spring cantilever, coupled with a capacitive displacement gauge. This enables us to measure the small strain shear modulus G as well as the total elastic energy $\mathcal{E}(\Delta h)$ stored in the sample [9].

The sample is then notched in the middle of one of its edges with a razor blade and loaded by a displacement $\Delta h \leq \Delta h_{\text{max}}$ such that a crack grows from the notch in the middle of the sample (see Fig. 1). Wet crack experiments are performed by adding a drop ($\simeq 50\text{ }\mu\text{L}$) of the gel solvent into the crack tip with a micropipette. Due to capillarity, the drop follows the crack tip during its propagation. Solvent losses due to evaporation and wetting of the crack faces are low enough for the crack tip to remain wet during the whole run.

The sample aspect ratio ($L \gg h$) is such that the loading configuration is the “pure shear test” one [14]. Accordingly, the energy

Table 1

Characteristics of the samples used in this study. Gels contain a weight fraction c of gelatin. A solvent with a volume fraction ϕ of glycerol in water has a viscosity η . The shear modulus of the gel at $T = 20\text{ }^\circ\text{C}$ is G from which the mesh size ξ is estimated according to $G = k_B T \xi^{-3}$ with k_B the Boltzmann constant. The characteristic poroelastic velocity is $V_{\text{poro}} = D_{\text{coll}}/\xi$ with D_{coll} the collective diffusion coefficient.

c [wt.%]	ϕ [%]	η [mPa s]	G [kPa]	ξ [nm]	D_{coll} [$10^{-11}\text{ m}^2\text{ s}^{-1}$]	V_{poro} [mm s $^{-1}$]
5	0	1	2.5	12	2.5	2.1
5	60	11	4.5	9.7	0.4	0.4
10	0	1	9.4	7.6	2.7	3.6
15	0	1	15	6.4	2.9	4.4

release rate of the crack is uniform in a large region, away from the sample edges, where it can be approximated by $\mathcal{G}(\Delta h) = \mathcal{E}/L_e$. Note that, although physical hydrogels are known to relax stress, this expression assumes that no dissipation occurs in the bulk of the gel during crack growth. However, it has been shown [15] that, in gelatin gels, stress relaxation slows down as aging proceeds, with a characteristic time which scales with the aging time itself. As our samples are aged for a total of 17 h, keeping them loaded for durations shorter than a few minutes ensures that no significant stress relaxation occurs. Accordingly, no significant rate dependence or hysteresis is observed on the un-notched loading–unloading response.

The loading Δh is decreased or increased stepwise in order to scan different values of \mathcal{G} . The crack is followed by recording its propagation with a video camera. From the tracking of the crack tip position $x(t)$ at constant Δh from the video record, we check that the crack grows at a constant velocity $V = dx/dt$ and we thus have access to the gel fracture energy $\Gamma(V) = \mathcal{G}(\Delta h)$ for dry and wet cracks on the same sample.

The collective diffusion coefficients D_{coll} of the gels were measured by dynamic light scattering [16] on samples having experienced the very same thermal history as the corresponding fractured ones: the temporal autocorrelation function of the intensity of a krypton laser beam scattered at a wave-vector \vec{q} is found to decrease exponentially with a characteristic time τ . The relaxation rate τ^{-1} of the gel concentration fluctuations is measured to increase linearly with q^2 as expected for a diffusive mode [17], for which $\tau^{-1} = 2D_{\text{coll}}q^2$.

The physical characteristics of the different samples used in this study are shown in Table 1.

4. Experimental results

Fig. 2 displays the $\Gamma(V)$ characteristics of mode I cracks for $c = 5\text{ wt.}\%$ gelatin gels in pure water ($\phi = 0$). For each sample, the crack dynamics was assessed under dry and wet crack tip conditions. The high reproducibility of the data over $n = 5$ samples firmly establishes the main result of this study, namely the striking qualitative difference between the $\Gamma(V)$ curve for dry and wet cracks. First of all, at high enough crack velocities one recovers the previously reported behavior, namely both $\Gamma(V)$ characteristics are linear with identical slopes, the dry crack curve being merely shifted upwards from the wet crack one by a constant amount $\Delta\Gamma^{(0)} \simeq 1.6\text{ J m}^{-2}$. However, whereas the data for wet cracks remain remarkably aligned over the whole experimental velocity range $0.01 < V < 10\text{ mm s}^{-1}$, a systematic deviation from linearity is observed for dry cracks at low velocities $V < V^* \simeq 1\text{ mm s}^{-1}$. This can be described conveniently by a velocity-dependent hydration shift factor $\Delta\Gamma(V) = \Gamma_{\text{dry}}(V) - \Gamma_{\text{wet}}(V)$ with $0 < \Delta\Gamma < \Delta\Gamma^{(0)}$. Dry cracks are therefore weaker and weaker as their velocity decreases, their toughness approaching that of wet crack ones as $V \rightarrow 0$. This suggests that nominally dry cohesive zones get partially rehydrated at low enough velocities.

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