Delayed Fracture of an Inhomogeneous Soft Solid

Daniel Bonn,* Hamid Kellay, Michaël Prochnow, Karim Ben-Djemiaa, Jacques Meunier

The spontaneous fracture of polymer gels was studied. Contrary to crystalline solids, where fracture usually happens instantaneously at a well-defined breaking strength, the fracture of a polymer gel can occur with a delay. When a constant force was applied, the cracks nucleated and started to propagate after a delay that can be as long as 15 minutes, depending on the force. This phenomenon can be understood by calculating the activation energy for crack nucleation in arbitrary dimension and accounting for the inhomogeneity of the gel network in terms of its fractal dimension.

The spontaneous failure of materials under stress is, despite its great importance for everyday life, still ill understood (*1*, *2*). Usual fracture experiments either determine a fracture threshold stress by increasing the stress until the material breaks or study fatigue, that is, fracture resulting from the application of a cyclic load (*1*, *2*). Instead of varying the stress in time, we studied the spontaneous failure of gels subject to a constant permanent load. We show that the energy for the spontaneous nucleation of the initial fracture determines the lifetime of the unbroken material.

The polymer gels we used are viscoelastic materials that consist of a polymer network dispersed in water. We used three different physical gels, all consisting of cross-linked networks of agarose polymers of different length and cross-linking density. These gels are tough; rheological characterization shows that their elastic (storage) modulus is an order of magnitude larger than their viscous (loss) modulus (Fig. 1A). Hence, the response of the material to an applied deformation is primarily elastic (*3*).

We present here three-point flexion experiments, in which the two ends of a rectangular gel bar were supported and a known and controlled force F was applied at its center (Fig. 2). A linear relation between force and deformation was found (Fig. 1B), without much plastic deformation on the time scale of the measurement. This linear relation permits the evaluation of the Young's modulus E of the gels (*3*); for all three gels, we found $E \approx 50$ kPa. Applying a constant force to the gel bar, we found that breaking does not occur instantaneously but happens after a certain delay time. For a given force, the distribution of the time after which the gel breaks is a Poisson distribution (Fig. 3). This distribution demonstrates the random nature of the fracture process and allows one to define a mean breaking time t_b. By changing the force, we found that t_b is an extremely steep function of F. For example, changing the force from 300 to 550 mN led to a change in t_b of almost two orders of magnitude, from 15 min to 20 s.

If an energy barrier for nucleating a crack exists and the nucleation is thermally activated, t_b should be inversely proportional to the nucleation probability $P \sim \exp(-E_{act}/k_BT)$, where E_{act} is the activation energy, k_B is Boltzmann's constant, and T is the temperature. Although our experimental window was very limited because of the steep dependence of t_b on F, it appears that E_{act} shows a power-law dependence on F (Fig. 4A).

It has previously been suggested by Griffith (*4*) that such an energy barrier might exist for the nucleation of a crack. The activation energy results from a competition between the cost in fracture (surface) energy and the gain in elastic (volume) energy for the formation of the initial crack. In two dimensions, the energy cost E_s depends linearly on the crack length L and is given by $E_s \approx \Gamma L$, where Γ is the fracture energy. The elastic energy gain E_v is qua-

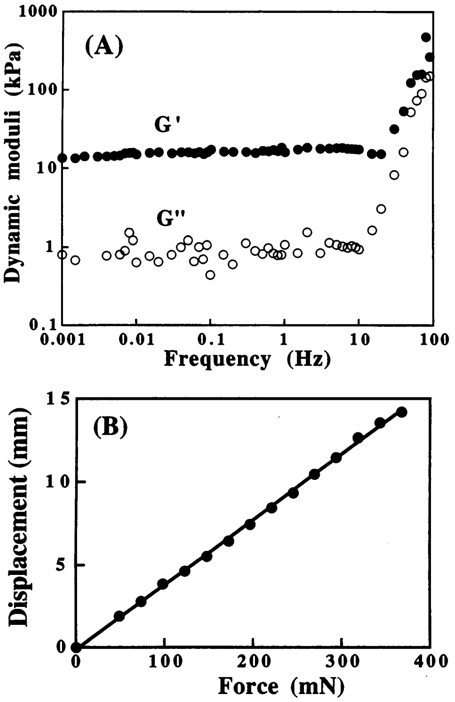


Fig. 1. (**A**) Rheological determination of the storage modulus G' and the loss modulus G'' as a function of frequency. (**B**) Determination of Young's modulus E from the slope of the force versus deformation curve in the three-point flexion experiment.

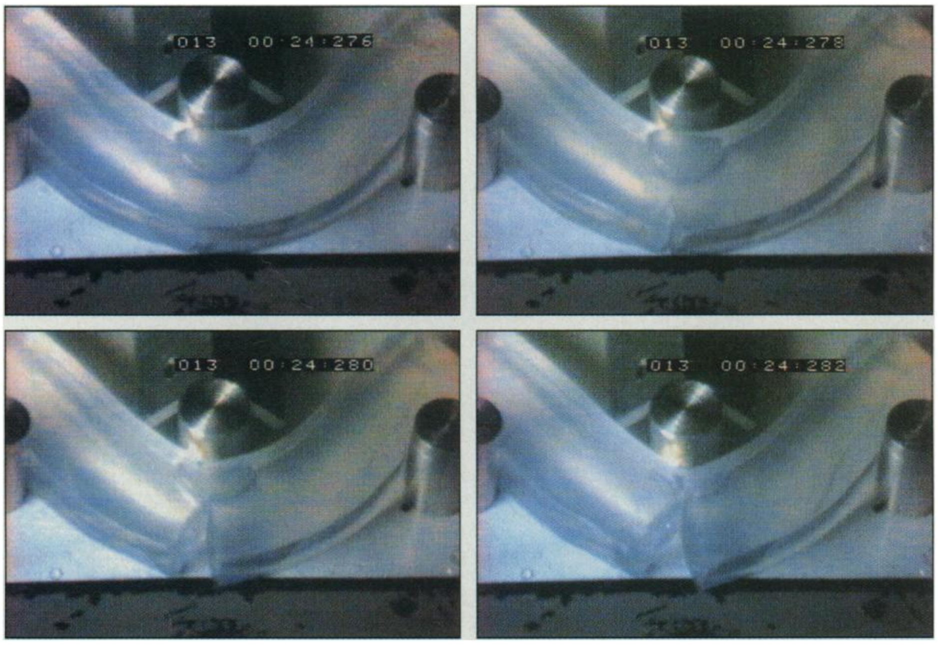


Fig. 2. High-speed photography pictures of the crack propagation. The time between each image is 2 ms.

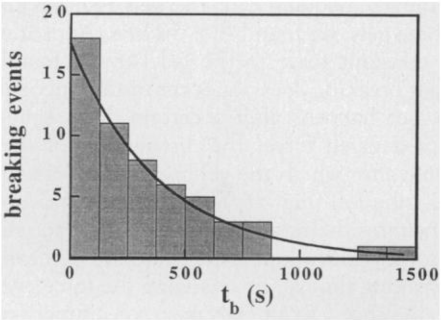
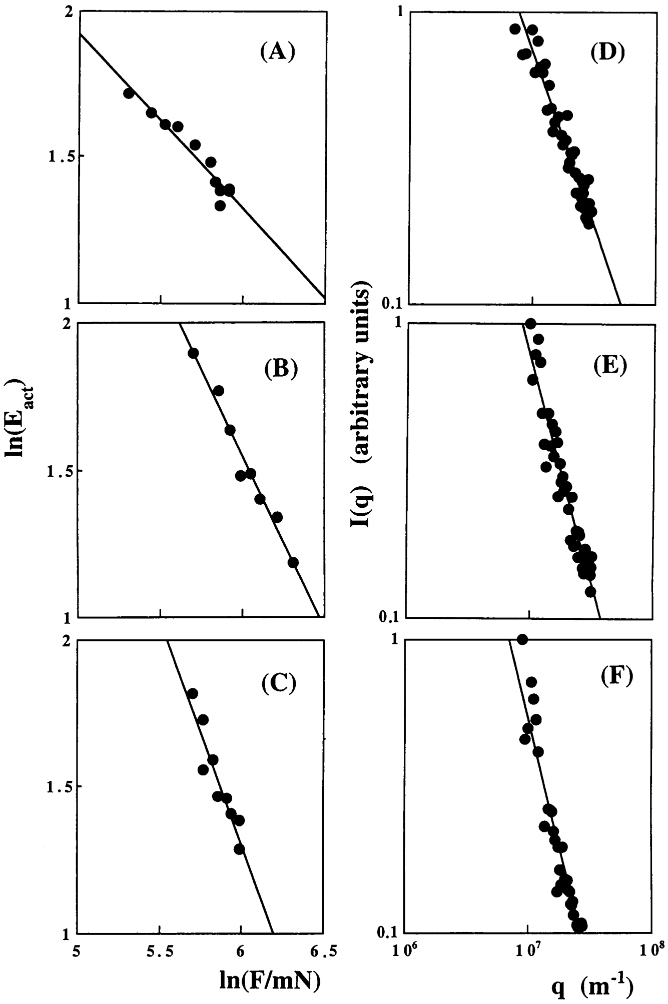


Fig. 3. Distribution of t_b for a large number of experiments at a constant force of 250 mN; the curve is a Poisson distribution.

Fig. 4. (**A** to **C**) The activation energy (expressed as the natural logarithm of the breaking time in seconds) as a function of the applied force on a logarithm-logarithm scale. The straight lines are fits to a power-law dependence. Data are for gels 1 (A), 2 (B), and 3 (C). (**D** to **F**) The light-scattering intensity $I(\mathbf{q})$ (normalized to 1 at the smallest wave vector) as a function of the scattering wave vector **q**. The straight lines are power-law fits that yield the fractal dimension of the gels. The scales for the three gels are identical. Data are for gels 1 (D), 2 (E), and 3 (F).



dratic in L according to $E_v \approx \sigma^2 L^2/E$, where σ is the stress, which is proportional to the applied force. The activation energy then follows from extremalization of the total energy: $E_{act} \approx \Gamma^2 E/\sigma^2$. This equation shows that a power-law dependence of E_{act} on σ and hence on F can be expected, which has been used successfully to account for the fracture of two-dimensional crystals (*5*).

An extension of the calculation to the three-dimensional case has been proposed by Pomeau (*6*). The basic assumption is that the extension of the initial (critical) crack in the third dimension is also of order L. The same calculation then leads immediately to the conclusion that a delayed fracture is not observable in three dimensions; extremalization leads to $E_{act} \approx \Gamma^3 E^2/\sigma^4$. The lifetime depends exponentially on the activation energy, and thus the dependence on the force is simply too steep to be observed experimentally. This result agrees with everyday experience: A (brittle) solid body usually breaks instantaneously or does not break, depending on the force. Generalizing this same argument to arbitrary dimensionality d of the system, we found $E_{act} \approx \Gamma^d E^{d-1}/\sigma^{2d-2}$, implying that the power-law dependence of E_{act} on F is determined by the dimension of the system. That the activation energy depends on dimension is not surprising because it is determined by the ratio of the number of bonds that need to be broken to those that relax their elastic energy.

The correct way of "counting" these numbers of bonds of the gels is to account for the inhomogeneity of the polymer network. The inhomogeneity of agarose gels was studied in much detail recently; it was found that the gel network can be well characterized as a fractal over the range of length scales covered by visible light scattering (*7*). Although the fractality obtained in this way only extends over roughly a decade in length scales, we still refer to the gels as being fractal (*8*). We determined their fractal dimension by static light scattering. For mass fractals, a power-law dependence of the wave vector–dependent scattered intensity $I(\mathbf{q})$ is observed (*9*), and the absolute value of the power equals the fractal dimension d_f. For the different gels, we obtained fractal dimensions in the range of 1.2 to 1.8 (Fig. 4B), which shows that the gels probably form by an aggregation process that limits the range of fractal dimensions that one can obtain (*9*).

Although the length scale probed by visible light is the relevant one for the fractal behavior (*7*), it is not evident that this scale is also the relevant one for the nucleation process. We therefore measured the fracture energy by studying the breaking strength of samples with a small notch at the point at which the crack normally starts. By determining the critical stress intensity factor (given by the stress at which the gel breaks) as a function of the length of the notch, the fracture energy can be determined (*10*). We found $\Gamma = 155$ mN m^{-1}, twice the surface tension of water, which is a reasonable value because the sample consists predominantly of water, showing also that there is an important contribution to Γ from the polymer network. The critical crack length L_c is the length at which the energy is extremal; from the above arguments, $L_c = 2(d-1)\Gamma E/d\sigma^2$, again up to numerical factors of order one identical to the classical result (*1*, *2*). Putting in values for E and Γ, we found L_c to be typically on the order of 0.1 μm, exactly the same length scale probed by the light-scattering experiments.

The power-law exponent of E_{act} versus F depends linearly on the d_f of the gels (Fig. 5), in agreement with the scaling arguments given above. We thus observe a direct relation between the (fractal) dimension of the system and the time at which the structure fails.

An alternative explanation for the delayed fracture could be that the materials

---

D. Bonn, M. Prochnow, K. Ben-Djemiaa, J. Meunier, Laboratoire de Physique Statistique de l'Ecole Normale Supérieure, 24 rue Lhomond, 75231 Paris Cedex 05, France.
H. Kellay, Centre de Physique Moléculaire Optique et Hertzienne, Université Bordeaux 1, 351, Cours de la Libération, 33405 Talence, France.

*To whom correspondence should be addressed. E-mail: bonn@physique.ens.fr

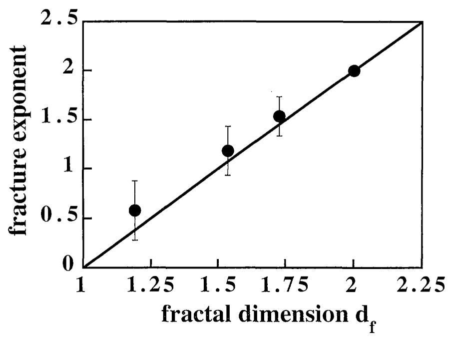


Fig. 5. The absolute value of the measured exponent of activation energy versus force as a function of the fractal dimension of the gels. The point at $d_f = 2$ is the measurement of (*5*) for a two-dimensional crystal. The line is the prediction from the scaling arguments presented in the text.

are visco-elastic and thus have an inherent relaxation time. However, the three different gels have practically the same visco-elastic moduli, in spite of the observed large difference in their fracture behavior. Moreover, as is evident from Fig. 1A, no visco-elastic relaxations were found for low frequencies. These low frequencies equal the inverse of the measured t_b; the important visco-elastic relaxations occur at much higher frequencies, higher by several orders of magnitude. Third, the results for the two-dimensional single crystals also agree with the findings for the gels.

A fracture that propagates very slowly and suddenly becomes unstable, a so-called creep fracture, would be another explanation for our experimental results (*11*). A typical example is a small crack in a windshield; it does not propagate because the crack front is trapped on impurities in the material. In studying the fracture dynamics of the gel with high-speed photography (Fig. 2), we sometimes saw this lattice trapping, but it never lasted longer than a fraction of a second. Thus, the energy barriers involved in lattice trapping are much smaller than the barrier for the nucleation of the initial crack, and it seems unlikely that this mechanism applies. More generally, our results cannot be understood by considering a distribution of preexisting flaws that grow and lead to the failure of the material, because in the three-point flexion geometry of our experiment, the initial crack always starts to propagate opposite to where the force is applied.

We have demonstrated and explained the existence of a delayed fracture in an inhomogeneous soft solid. These results should be relevant for the food industry (*12*), in which polymer gels are widely used. However, they could also have implications for the strength of a larger class of composite materials such as two-phase or polycrystalline materials, the fracture properties of which have only been described phenomenologically (*2*, *13*).

REFERENCES AND NOTES

1. L. B. Freund, *Dynamic Fracture Mechanics* (Cambridge Univ. Press, Cambridge, UK, 1990).
2. M. F. Kanninen and C. H. Popelar, *Advanced Fracture Mechanics* (Clarendon, Oxford, 1985).
3. Agarose type XII, I-a, and III-a (denoted as gels 1, 2, and 3) from Sigma was dissolved at 1 weight % in water (Milli-Q-Plus) at 95°C by stirring. Subsequently, the solution was poured into a mold and left for at least 2 hours at 20°C before use. For the three gels, we found E = 75.2, 46.1, and 50.6 kPa. For $\sigma < 50$ Pa or frequency $f < 10$ Hz, the elastic or storage modulus $G' = 22.8$, 14.6, and 15.6 kPa, respectively. As expected for a gel, Poisson's ratio ≈ 0.5. The ratio of G' and the viscous or loss modulus G'' (G'/G'') is between 10 and 13 for the three gels. Rheological measurements were performed on a Reologica Stress-Tech rheometer. For the fracture experiments, a rectangular bar (100 mm × 20 mm × 10 mm) rested on a Teflon-coated surface greased with liquid Vaseline oil, with its ends held in place by two aluminium rods. The middle flexion point moved on an air bearing and was coupled to a force transducer. A small amount of plastic deformation was observed for the largest forces; in the experiments, the force was always kept constant. Plastic deformation due to aging was not observed in the experiments.
4. A. A. Griffith, *Philos. Trans. R. Soc. London Ser. A* **221**, 163 (1920).
5. L. Pauchard and J. Meunier, *Phys. Rev. Lett.* **70**, 3565 (1993).
6. Y. Pomeau, *C. R. Acad. Sci. Ser. II* **314**, 553 (1992).
7. M. Manno and M. U. Palma, *Phys. Rev. Lett.* **79**, 4286 (1997).
8. D. Avnir, O. Biham, D. Lidar, O. Malcai, *Science* **279**, 39 (1998).
9. D. A. Weitz, J. S. Huang, M. Y. Lin, J. Sung, *Phys. Rev. Lett.* **54**, 1416 (1985).
10. J. Zarzycki, *J. Non-Cryst. Solids* **100**, 359 (1988).
11. M. Marder, *Phys. Rev. E* **54**, 3442 (1996).
12. A. Bot, R. D. Groot, W. G. M. Agterof, in *Gums and Stabilizers for the Food Industry 8*, G. Phillips, P. Williams, D. Wedlock, Eds. (IRL, Oxford, 1996), pp. 117–126.
13. B. Lawn, *Fracture of Brittle Solids* (Cambridge Univ. Press, Cambridge, UK, 1993).

14. We thank M. Adda-Bedia for helpful discussions and V. Bergeron (Rhone-Poulenc) for the use of the high-speed camera. Laboratoire de Physique Statistique de l'Ecole Normale Supérieure is Unité de Recherche Associée 1306 of the CNRS, associated with Universities Paris 6 and 7.

26 November 1997; accepted 19 February 1998

Thermographic Selection of Effective Catalysts from an Encoded Polymer-Bound Library

Steven J. Taylor and James P. Morken*

A general method is introduced for the rapid and simultaneous evaluation of each member of large encoded catalyst libraries for the ability to catalyze a reaction in solution. The procedure was used to select active catalysts from a library of potential polymer-bound multifunctional catalysts. From $\sim$7000 beads screened (3150 distinct catalysts), 23 beads were selected for catalysis of an acylation reaction. Kinetic experiments indicate that the most strongly selected beads are also the most efficient catalysts.

In the development of new catalysts, many iterations of design and redesign are usually required to increase catalyst activity. Accordingly, many research groups have begun to use combinatorial chemistry (*1*) and solid-phase synthesis (*2*) to rapidly produce large numbers of potential catalysts. Despite recent progress in evaluating the thermodynamics of equilibrium processes involving polymer-bound libraries (*3*), methods for assessing the kinetics of reactions involving polymer-bound reagents have not been available. This circumstance has prevented the analysis of very large libraries (10^4 to 10^6 members), because screening for small-molecule catalysts requires an individual assay for each member of a catalyst library. Here, we report the development of a general single-pot assay for large, encoded polymer bead–bound catalyst libraries, which we used to select active catalysts from $\sim$7000 encoded catalyst beads (3150 different catalysts) prepared through "split and pool" solid-phase synthesis. This method is directly applicable to libraries of larger size.

Most chemical reactions have a measurable heat of reaction ΔH_r°, and thus temperature T has been used to survey the progress of catalytic reactions (*4*). Because all catalysts in a parallel library assay are evaluated under the same reaction conditions, the most active catalyst will cause the largest temperature change ($\Delta T \propto$ turnover frequency $\times\ \Delta H_r^\circ$). Recent advances in two-dimensional real-time infrared (IR) thermography have made spatial resolution of temperature possible through measurement of blackbody radiation. Therefore, IR thermography may be used to simultaneously compare the rate of each reaction, in an array of reactions, by measuring the relative reaction temperatures. This concept was imaginatively used

---

Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599–3290, USA.

*To whom correspondence should be addressed. E-mail: morken@unc.edu