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First Observation of Stick−Slip Instability in Tearing of Poly(vinyl alcohol) Gel Sheets

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The fracture of gels has drawn much attention from researchers for several reasons. (1) The fracture strength of gels reflects the nonlinear mechanical behavior of polymer networks under very high stress.[1,2] Such behavior cannot be studied using conventional rheological techniques, and thus fracture of gels is of interest to polymer physicists. (2) Gels serve as model systems for the study of the detailed structure[3,4] and dynamic behavior[5] of crack fronts because crack propagation in gels is much slower than in hard solids. (3) New hydrogels with both high water contents and high mechanical toughness have been developed by some research groups.[6−8]

Chemically cross-linked poly(vinyl alcohol) (PVA) gels have been widely used for various applications such as the fabrication of soft contact lens because PVA gels have high biocompatibility and high transparency. However, the fracture behavior of these gels has never been systematically investigated. In this paper, we report the tearing behavior of thin sheets of chemically cross-linked PVA gels. We found that the crack front undergoes a repetitive rest and quick propagation cycle, and the plot of the tearing force versus time has a sawtooth profile. In addition, a quasiperiodic pattern was observed on the fracture surfaces. We interpret this unsteady tearing as a type of stick−slip instability of the crack fronts.

Poly(vinyl alcohol) (PVA) gels were synthesized from linear PVA (degree of polymerization: 2000; Wako Pure Chemical Industries, Japan) and a cross-linker of glutaraldehyde (Kanto Chemical Co., Japan). The cross-linking reaction was catalyzed by HCl[9] at room temperature. The concentration of PVA in the pregel solution was 10 wt %, and that of the cross-linker was 10 mol % with respect to the monomer unit of PVA. The concentration of HCl was 0.055 wt %. The pregel solution was poured (and sealed) in a mold consisting of a pair of glass plates and a silicon spacer with a thickness of 0.5 mm and left in the mold for 3 days at room temperature. In the course of the cross-linking reaction, the gel gradually shrunk (also low-viscosity solvent was left in the reaction mold). Subsequently, the gel was soaked in a large amount of water to remove reaction residuals. The volume of the gel was hardly changed in the soaking treatment. The thickness of the gel sheet after the soaking was 0.34 mm.

Figure 1a shows the experimental setup for the tearing measurement; it consists of an electrical balance (functioning as a sensitive force gauge), a small water bath containing the specimen, and a dc motor to drive tearing. Figure 1b shows the structure of the specimen. A pair of aluminum plates sandwiched the gel sheet, leaving a part of the gel (20 mm × 10 mm) outside the plates. The plates were attached to the inner wall of the water bath (the plates were tilted at 45° from the horizontal plane). An initial notch (length: 5 mm) was made on the gel sheet by using a razor, and one end of the gel sheet was pulled up by using a thread at a constant velocity V, as shown in Figure 1b (the thread was glued to the gel with adhesive). The force acting on the electrical balance was recorded using a personal computer; the tearing force $F(t)$ was determined from the decrease in the apparent weight of the water bath. Measurements were carried out at room temperature.

Figure 2a shows the variation in the tearing force F with time t ($V = 0.013$ mm/s). The inset shows a magnified section of the $F(t)$ curve. The $F(t)$ curve exhibited sawtooth oscillation. When the slope of the $F(t)$ curve was positive (see the inset), the crack front remained stationary and the deformation around the front was increased by the pulling action. The decrease in $F(t)$, on the other hand, corresponded to the quick propagation of the crack front. Figure 2b shows the $F(t)$ curve at $V = 0.13$ mm/s. The oscillatory tearing mode was observed for a wide range of pulling velocities V (at least from 0.0026 to 0.52 mm/s). A characteristic pitch pattern corresponding to the oscillatory tearing was formed on the fracture surfaces as shown Figure 2c. Two illustrations in Figure 2c represent the typical morphologies left on the fracture surfaces (a characteristic crack front structure (τ-structure) observed in previous investigations[3,4] seems to be involved in the formation of the pitch pattern). The pitch distance ranged from 0.1 to 0.5 mm, and the average distance between pitches was ~0.2 mm. With increasing V, the pitch pattern got somewhat disordered, but the characteristic scale of the pattern (i.e., pitch distance) was insensitive to V.

Figure 3 shows a plot of the average fracture energy G vs the pulling velocity V; G was determined by using $G = F_{av}/2b$, where F_{av} is the time average of $F(t)$ and b ($= 0.34$ mm) is the thickness of the gel sheet. G is insensitive to changes in V for large values of V (except a small peak at $V = 0.35$ mm/s that might be an artifact) but increased with a decrease in V for small values of V.

Phenomenologically, the oscillatory tearing is similar to the stick−slip motion observed in various sliding friction systems.[10] A typical example of stick−slip motion is the dragging of a solid block on a flat substrate; when the block is connected to one end of a spring and the opposite end is pulled laterally at a constant velocity, the block motion is characterized by rest (stick) and slip. One of the conditions required for the stick−slip motion to occur is that the maximum static frictional force should be larger than the dynamic frictional force (this is the case for dry friction). According to the analogy between stick−slip motion and the tearing behavior, the tearing force for a stationary crack (corresponding to the maximum static frictional force) should be larger than the tearing force for a moving crack front. In other words, the fracture energy at zero crack velocity is larger than that at finite crack velocities. This would be reflected as the largest value of G appearing at the lowest value of V in Figure 3.

To the best of our knowledge, this is the first observation of stick−slip tearing in gels. We also performed tearing measurements on poly(acrylamide) gels but did not observe any stick−slip tearing. On the other hand, Greensmith and Thomas have reported a similar stick−slip tearing in natural rubber and GR-S

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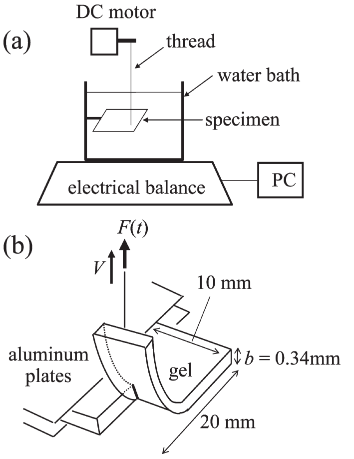

Figure 1. (a) Schematic representation of the experimental setup. (b) Illustration of the specimen consisting of a pair of aluminum plates clamping a PVA gel sheet.

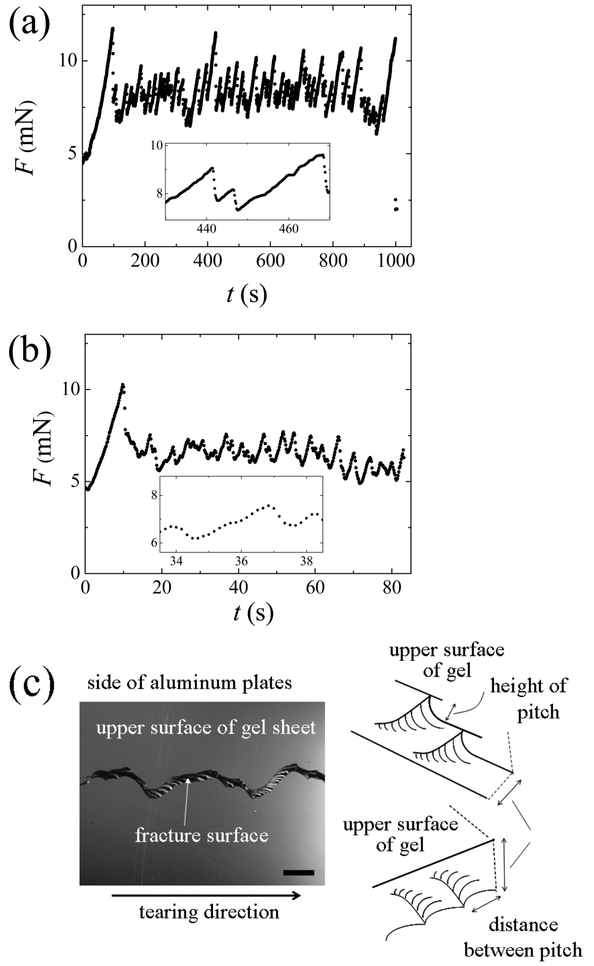

Figure 2. (a) Plot of $F(t)$ at a pulling velocity of $V = 0.013$ mm/s. (b) Plot of $F(t)$ at $V = 0.13$ mm/s. (c) Photographic image of a torn gel sheet at $V = 0.52$ mm/s (the scale bar represents 1 mm). A characteristic pitch pattern can be seen on the fracture surface. Right illustrations represent typical morphologies of the fracture surface. The upper and lower morphologies are made at the same time on the opposite sides of the crack front (they are in the relation of "foot and footprint").

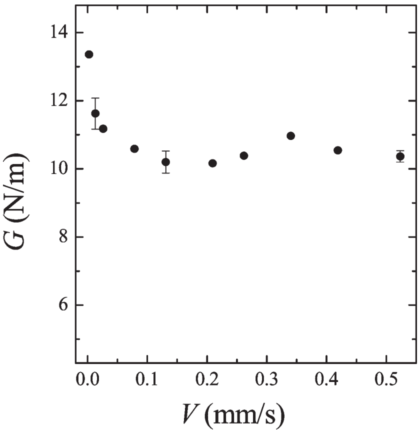

Figure 3. Plot of the G vs V. G is defined as the averaged tearing force divided by twice the gel thickness. The error bars represent the standard error of three repeated measurements.

vulcanizates.[11] Their explanation for stick−slip tearing (or the negative dependence of tearing force on crack velocity) is that strong stretching in the vicinity of the crack front (so-called process zone) induces an ordered structure (crystallization, etc.) that is tougher but forms very gradually. It is quite likely that also for the case of our PVA gel strain crystallization occurs in the vicinity of the crack front because PVA is capable of forming crystalline domains through strong hydrogen bonds.[12,13] For the crystalline domains to grow in the gel, water should be squeezed out. Relaxation processes relating to the squeeze and transport of water would determine the characteristic time scale of the toughening.

To summarize, we carried out tearing measurements on chemically cross-linked PVA gel sheets and found the occurrence of an oscillatory tearing behavior similar to stick−slip motion in dry friction systems. This indicates that the tearing force (or fracture energy) for stationary cracks is larger than that for moving crack fronts. A possible mechanism underlying this tearing behavior is the formation of crystalline domains by strong deformation in the vicinity of crack tips. Detailed analysis for this novel phenomenon will be reported elsewhere as a separate study.

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