

Fracture Energy of Acrylamide Gel

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We investigated dependence of fracture energy G of acrylamide (AA) gel on crack speed V . Four kinds of AA gels which have same polymer concentration and different cross-link densities were used in this study. In a fast V region ($V > 1\text{cm/s}$), G of the gels linearly increases with V . Both the value of G at a given value of V in the region and the increasing rate of the fracture energy dG/dV decrease with increasing the cross-link density. In the slow crack speed region ($V < 1\text{cm/s}$), G depends on V more strongly than in the fast V region. This indicates that a qualitative change exists in fracture process of the gels.

Key words: Acrylamide gel, Fracture, Peel test

1. INTRODUCTION

Although various phenomena in gels such as gelation, deformation and phase transition have been extensively studied [1,2], few studies have been carried out on fracture of gels[3-5]. Nevertheless, in the field of polymer physics, fracture of gels can be an interesting topic. Firstly, we have useful concepts to understand static and dynamic properties of gels, for example, the coupling between stress and polymer concentration[2] or the cooperative diffusion mode[1]. To test applicability of the concepts to fracture phenomena is important in study of gels. Secondly, fracture of gels distinctly has connections with other topics in polymer physics such as fracture of rubbers[6] and adhesion of polymeric liquids[7]. It is meaningful to clarify similarity and difference between these topics.

Here we report fracture energy measurement on the four kinds of acrylamide(AA) gels which have the same polymer concentration and different cross-link densities[8]. Generally the fracture energy is determined by microscopic process near crack fronts and appears in macroscopic descriptions of fracture as an important parameter. Thus, the fracture energy is an essential physical quantity to understand the nature of fracture in gels. We have developed a novel method suitable for studying fracture energy of gels by which we can measure the fracture energy of gel G as a function of crack speed V . Main points of our result are i) $G(V)$ for each cross-link density linearly increases with V for fast values of V ($V > 1\text{cm/s}$) and the value of $G(V)$ at a given V decreases with cross-link density ii) At slow values of V , an instability occurs, where negative dependence of G on V and roughening of fracture surfaces are observed. We also investigated the roughening and related it to the observed fracture energy.

2. EXPERIMENT

We use as samples four kinds of acrylamide gels which have same polymer concentration and different cross-link densities. The amount of each reagent for preparing acrylamide gels is shown in Table 1. We will distinguish the samples by the codes of 4BIS - 10BIS as

shown in Table 1. The values of Young's modulus E which were measured by compressing the gels are also shown in Table 1.

In Fig. 1 we present a gel fractured by the method. We fixed the gel on an aluminum plate and made an initial notch and attached a filter paper to the upper surface. By pulling-up the filter paper vertically at a constant speed V , a thin layer of the gel ($\sim 1\text{mm}$) was peeled off and the crack propagated through the gel at the rate V . The force needed in pulling-up $F(t)$ was measured with a strain-gauge.

Fracture energy G is defined as the energy needed to make a unit area of a fracture surface. In our peel-test like method the fracture energy G is calculated by the following equation,

$$G = \frac{F}{w}, \quad (1)$$

where F is the measured force and w is the width of the pillar-shaped gel (see Fig. 1). In this study we evaluate the roughness of the fracture surfaces using replicas produced by molding the fracture surfaces using silicon rubber. A quantity that can be regarded as a measure of the roughness of the fracture surfaces was extracted from the image of the cross section.

3. RESULT

Figure 2a is $F(t)$ at $V = 0.4\text{cm/s}$. The arrows indicate the initiation and the termination of the fracture propagation. The fracture propagates steadily in the period of time between the arrows. We evaluated the fracture energy G using the time average of $F(t)$ for a

| Sample code | Water | AA | BIS | E(10^4Pa) |
|-------------|-------|-----|-------|----------------------|
| 4BIS | 100cc | 10g | 0.04g | 0.56 |
| 6 BIS | 100cc | 10g | 0.06g | 1.21 |
| 8 BIS | 100cc | 10g | 0.08g | 1.86 |
| 10 BIS | 100cc | 10g | 0.1g | 2.77 |

Table 1 The composition of the four kinds of acrylamide gels and Young's of them

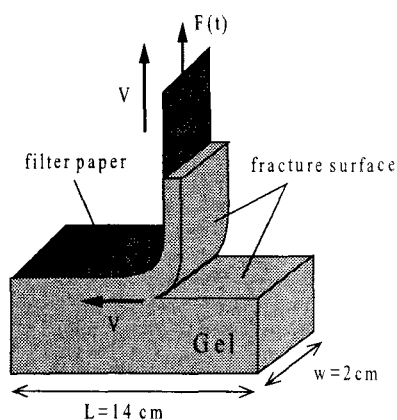


Fig. 1 A schematic of a gel undergoing fracture.

central part of the period. Figure 2b is $F(t)$ at $V=0.04$ cm/s. As shown in Fig.2a there is a period of time corresponding to the steady fracture propagation. However the fluctuation of $F(t)$ in Fig.2b is larger than that in Fig.2a even in the period of the steady state fracture propagation. The increase in fluctuation of $F(t)$ is accompanied with roughening of fracture surfaces. We explain the roughening of fracture surface in detail later (see Fig.5 and Fig.6).

Figure 3 is a plot of the fracture energy G as a function of crack speed V . At fast values of V ($V > 1$ cm/s), $G(V)$ depends linearly on V and both $G(V)$ and dG/dV decrease with increasing BIS concentration of the samples. Figure 4 is a plot of the fracture energy $G(V)$ of 4BIS, 6BIS and 8BIS for $V < 1$ cm/s. A common feature of $G(V)$ for these samples is that there is a region of V where G increases with decreasing V and $G(V)$ has a minimum (shown by the upward arrows in Fig. 4) at a value of V . Hereafter, we will call this V_{min} .

As V decreases across V_{min} , the roughness of the fracture surfaces grows up (*the roughening at slow fracture*). In Figures 5a-c we show the morphologies of fracture surface of 6BIS at different crack speeds. Figures 5e-g show the cross sections of the fracture surfaces shown in Figs.5a-c, respectively. The cross section is along the plane that is perpendicular to the global fracture surfaces and contains the centerlines of the fracture surfaces (the x-axis in Fig.5d). The

vertical size of the cross section corresponds to 3cm and the horizontal size is magnified 2.5 times compared with the true scale. The shape of right-hand side boundary of the cross-section corresponds to the $h(x)$ shown in the illustration, i.e., the height of the fracture surface measured at each point of the x-direction. Figure 5a is a fracture surface of 6BIS above V_{min} . At such crack speeds most parts of fracture surface are flat and a few steps exist on the global fracture surface, which seem like lines in Fig.5a. Around V_{min} , such steps are frequently produced and the roughness of the fracture surfaces begins to grow up (Fig.5b). As V decreases further, the roughness of the fracture surfaces becomes remarkable (Fig.5c).

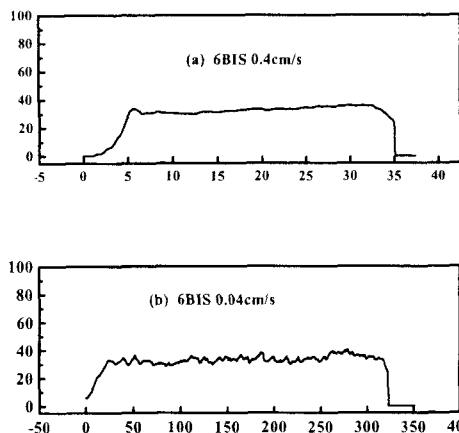


Fig. 2 (a) is an example of the measured peeling force $F(t)$ at $V=0.4$ cm/s. The arrows indicate the initiation and the termination of fracture. (b) is an example of $F(t)$ at $V=0.04$ cm/s. Fluctuation of $F(t)$ is larger compared with (a).

To quantify the roughness of the fracture surfaces we introduce a quantity R defined by the following equations.

$$R(V) = \frac{\int_{l_c} dx \sqrt{1 + (dh/dx)^2}}{\int_{l_c} dx} \quad (2)$$

where the range of integration l_c represents the distance along the x-axis which corresponds to the central period of time in which the average of $F(t)$ is took. The numerator on right-hand side in (2) is the contour length of $h(x)$ on the distance, thus R is equal to 1 for the completely flat fracture surface ($dh/dx = 0$) and increases from 1 as the roughness of the fracture surface increases. Therefore, R is an index of the roughness of the fracture surfaces.

In Fig. 6 we show R as a function of the crack speed V for the four kinds of sample gels. $R(V)$ of the gels has a common feature; i.e. at fast values of V , R is close to 1 and with decreasing V , R begins to increase at the value of V close to V_{min} . This fact clearly shows the correlation between the roughening of fracture surfaces and the increase in $G(V)$ with decreasing V across V_{min} .

When we take into account the roughness of fracture surfaces, we should correct the fracture energy by dividing it by R^2 . In Fig.7 and Fig.8, we show the corrected fracture energy $\underline{G}(V) \equiv G(V)/R(V)^2$. Behavior of $\underline{G}(V)$ at fast values of V is qualitatively identical to that of $G(V)$, i.e., $\underline{G}(V)$ linearly increases with V and $\underline{G}(V)$ and $d\underline{G}/dV$ decrease with BIS concentration. On the other hand, when V decreases, the crossover in $\underline{G}(V)$ occurs in the narrow range of V , and below the crossover $d\underline{G}/dV$ becomes larger than above the cross-over. As a result of the correction, $\underline{G}(V)$ at each value of V in the region monotonically depends on BIS concentration as in the fast V region. Our results for the corrected fracture

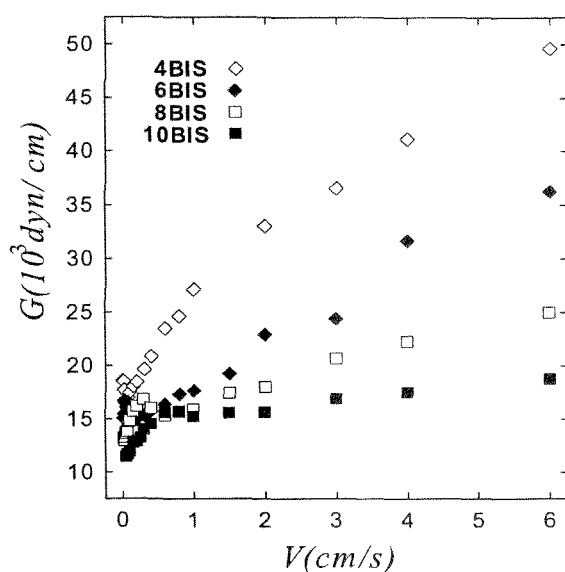


Fig. 3 The fracture energy $G(V)$. At fast values of V ($V > 1$ cm/s), $G(V)$ of each sample linearly increases with V .

energy \underline{G} can be summarized as follows:

- i) At a given value of V , $\underline{G}(V)$ decreases with increasing the BIS concentration.
- ii) At fast values of V ($V > 1$ cm/s), $\underline{G}(V)$ for each BIS concentration linearly increases with V .
- iii) With decreasing V across a cross-over range, $d\underline{G}/dV$ becomes larger.

4. DISCUSSION

We will discuss the corrected fracture energy \underline{G} . Hereafter we refer to \underline{G} merely as fracture energy and omit the under bar. As shown in Figs. 7-8, the order of the fracture energy $G(V)$ of the gels is several hundred times as large as that of the surface tension of water (about 0.072 N/m at 25[9]). Thus $G(V)$ reflects energy needed for breaking the network structure of the gels near crack fronts.

The following four factors participate in the fracture energy of gel G ,

- a) stretching partial chains in the gels,
- b) cutting the chemical bonds of the partial chains,
- c) pulling-out of cut and dangling chains,
- d) bulk viscoelastic loss.

The factors a), b) and c) are local processes near the crack tip, and the factors a), b) and d) are concerned with heat generation.

In the gels the factor a) always dominates the factor b) as discussed below. If we regard each partial chain between chemical cross-links or entangling points as the ideal chain, free energy U of a partial chain stretched up to a length x is given by $U \approx (k_B/Na^2) x^2$, where a is the size of the segment and N is the number of the segment in the partial chain, and the energy Uc of

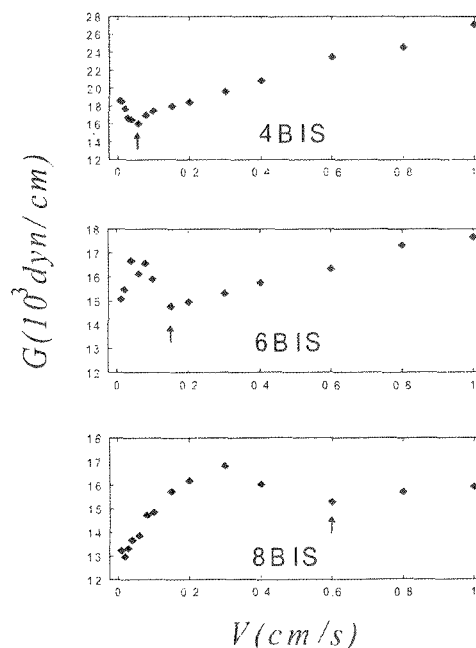


Fig. 4 $G(V)$ of 4BIS, 6BIS and 8BIS for $V < 1$ cm/s. $G(V)$ non-monotonically depends on V in the region and the minimum of $G(V)$ exists.

fully stretching ($x = Na$) is given by $Uc \approx N k_B T$. (This is probably an underestimation.) N is most likely of the order of several tens or more in the gels. On the other hand, the energy of C-C bond is on the order of a few times of $k_B T$ at room temperature, which is much smaller than the value of Uc . This is consistent with the result i).

Above discussion says the factor b) is a minor one compared with the factor a) (thus with the whole values of G). However, this does not mean the factor a) is dominant in G . What is the most dominant factor of a), c) and d)? How do the three factors relate each other? At present, we do not have reliable experimental evidences to answer these questions. With regard to the factor d), some theoretical studies[10,11] predicted that in viscoelastic materials, the observed fracture energy G is given in the following form except for very large or very small values of V ,

$$G = \lambda G_0, \quad (3)$$

where G_0 is the fracture energy in the usual mean, i.e., the energy due to the local processes and the dimensionless parameter λ , which is decided by the constitutive equations, does not depend on V . According to this theoretical viewpoint we may attribute the V dependence of G of the result ii) (not the absolute values of G) to the near tip processes of a) and c).

The physical meaning of the result iii) becomes clear if we exchange the ordinate and the abscissa of Fig. 7 and we recall that G is proportional to the force driving the fracture. Above the crossover range of V , an increase of the driving force G causes larger increase of V than below the critical value. One of the possible explanations for the crossover is that the near tip

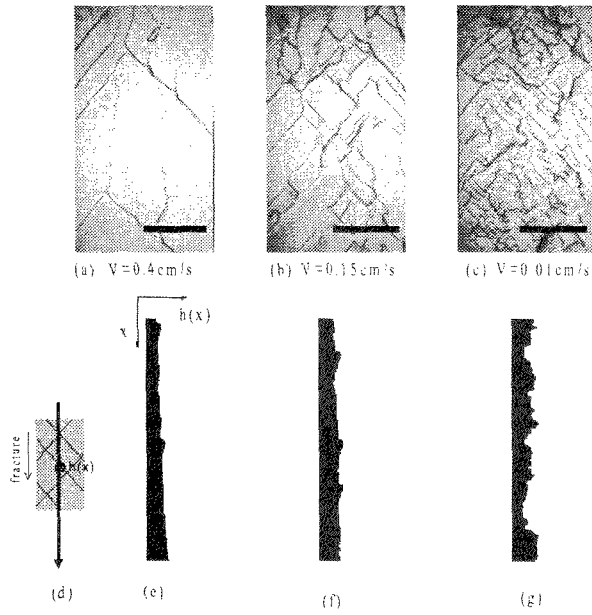


Fig. 5 (a)-(c): Examples of the fracture surfaces of 6BIS. The fracture propagated from top to bottom of each figure. The bars represent 0.9 cm. (d): An illustration of a fracture surface in which the x -axis and the profile of the height of fracture surfaces $h(x)$ are defined. (e)-(g): Cross sections of the fracture surfaces shown in (a)-(c), respectively. Shapes of the right-hand side boundaries of (e)-(g) represents $h(x)$.

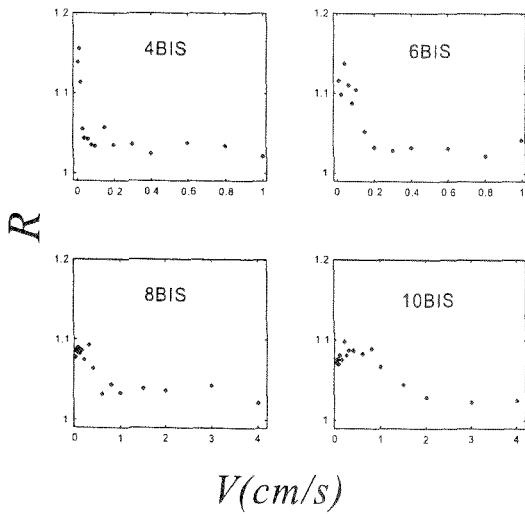


Fig. 6 An index of the roughness of fracture surfaces $R(V)$ defined by the equation (2) in the text. As V decreases, R begins to grow up. The value of V at which the R begins to grow up (indicated in Fig. 4 by upward arrows) corresponds to the value of V that gives the minimum of $G(V)$ in Fig. 4.

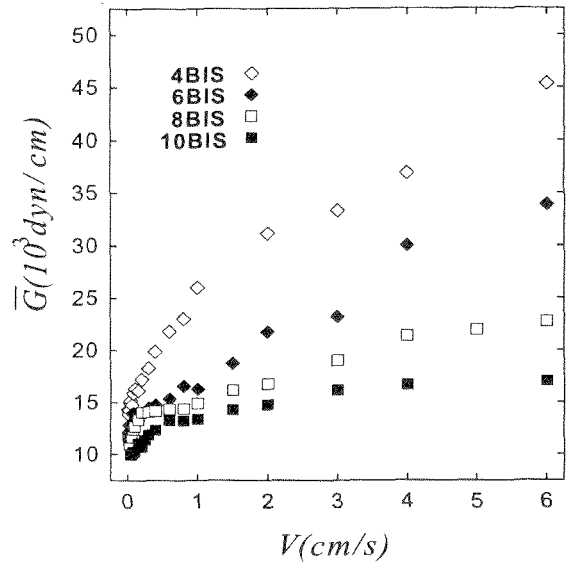


Fig. 7 The corrected fracture energy $\bar{G}=G/R^2$. At fast values of V , behavior of \bar{G} is qualitatively identical to that of $G(V)$.

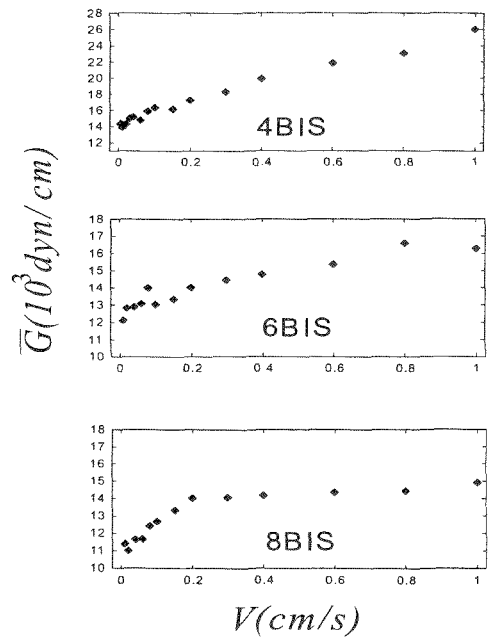


Fig. 8 \bar{G} of 4BIS, 6BIS and 8BIS for $V < 1$ cm/s. In this region \bar{G} monotonically depends on V . This is quite different from the behavior of $G(V)$ in Fig. 4.

processes themselves change qualitatively, for example, deformation of dangling chains reduces resistance in pulling-out the chains. Other possibility is that the crossover occurs depending on whether the viscoelastic loss arises (fast V side) or not (slow V side). When intending to study the near tip processes in detail, we encounter one of the common problems in study of gels, i.e., it is difficult to control or characterize the microscopic structures of gels. Nevertheless, we expect that we can get important information on the fracture of gels by combining the fracture energy measurement on better systems, for example, the gel into which a definite amount of linear polymers are introduced, and viscoelastic measurement on the systems. The study on this line is now underway.

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