

Effects of Cross-linking on Swelling, Mechanical and Fracture behavior of Gels

Yoshimi Tanaka and Noriyuki Tanigawa

Department of Mechanical Systems Engineering, Faculty of Engineering, Toyama Prefectural University
Kosugi-machi, Toyama 939-0398, Japan

Fax: 0766-56-6131, e-mail: ytanaka@pu-toyama.ac.jp

We investigate dependence of fracture energy of acrylamide gels on preparing cross-linker concentration; and relate it to mechanical and swelling properties. Behavior of the fracture energy qualitatively changes on a narrow range of the cross-linker concentration. Crossovers are found also in the Young's modulus and in the equilibrium swelling ratio. A reasonable explanation for the crossovers is the change in network topology of gels, i.e., the number of dangling chains and the number of constraints by a kind of entangling points.

Key words: gels, fracture energy, rheology, swelling

1. INTRODUCTION

Gels are very weak solids. This means two properties of gels: One is concerned with very small values of the Young's modulus; and the other is concerned with their fragility. One of objective quantities for evaluating whether a material is tough or fragile is the fracture energy G , which is defines as the energy needed in producing an unit area of fracture surface [1].

In previous study [2, 3] we investigated the effect of preparing cross-linker concentration on the fracture energy of acrylamide gels. The present study is an extension of the previous study; we change the cross-linker concentration more widely. A motivation of the extension is Furukawa's study [4] on swelling behavior of acrylamide gels. He found that the swelling behavior qualitatively changes depending on the preparing monomer and/or cross-linker concentrations; and interpreted the crossover as a consequence of difference in topology of network structure in the gels. The aim of the present study is to connect his findings to the fracture behavior of the gels. For this aim, we compare the swelling, mechanical (rheological) and fracture properties of the acrylamide gels which have same monomer concentration but different cross-linker concentrations. An important result of this study is that these three quantities qualitatively change at nearly same value of the cross-linker concentration.

2. EXPERIMENTAL

Samples— As in previous work, we used as samples a series of acrylamide gels that have same monomer concentration but different cross-linker concentrations. The amount of each reagent for preparing acrylamide gels is shown in Table 1. Acrylamide monomer (AA, $M_w = 71.08$) constitutes sub-chains and methylenebisacrylamide (BIS, $M_w = 154.17$) constitutes cross-links. Ammonium persulphate (APS) and N,N,N',N'-tetramethylenediamine (TEMED) are added to initiate and accelerate the radical polymerization of AA and BIS. We will distinguish the samples by the codes of A7.5B4 ~ A7.5B18 as shown in Table 1. To indicate BIS concentration briefly we introduce

Table 1: The sample codes and compositions of sample gels.

sample code	water	AA	BIS
A7.5B4	100cc	7.5g	0.04g
A7.5B6	100cc	7.5g	0.06g
⋮	⋮	⋮	⋮
A7.5B18	100cc	7.5g	0.18g

the quantity C_{BIS} by the number in the last part of the sample code of each gel, for example, C_{BIS} for the sample A7.5B10 is 10. The morality of each sample can be calculated by $C_{BIS} \times (0.1/154.17)$.

Measurement of the fracture energy $G(V)$ — The method for measuring $G(V)$ is identical to that of the previous work, the details of experiment are given in [2]. The top of Fig. 1 shows a gel in fracturing. The sample gel is fixed on an aluminum plate. A strip of filter paper is attached to the upper surface of the gel. The end of the filter paper is connected to a strain-gage through a wire. The strain-gage locates well above the gel (1.8m), and can be lifted up vertically by a linear-moving motor. The control parameter is the lifting up speed V which is equal to the crack speed V in this geometry of fracture. The measured quantity is the force $F(t)$.

The bottom of Fig. 1 is an example of measured force $F(t)$. The plateau region in $F(t)$ can be found, which corresponds with the steady-state fracture. The fracture energy $G(V)$ is defined as the energy needed in producing an unit area of fracture surface. $G(V)$ can be calculated from the time average $\langle F \rangle$ of $F(t)$ in the plateau region by the following equation:

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

where w is the width of the sample gels, which is 20mm in present study. In order to understand this relation, let us suppose that the crack front in Fig. 1 steadily propagates over a distance Δx along the direction of the longest

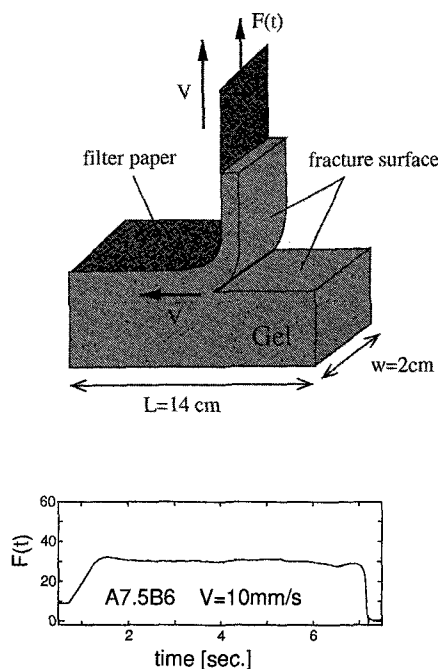


Fig.1: A fracturing gel (the top) and an example of $F(t)$ (the bottom). A plateau region can be seen in $F(t)$.

axis. The increase in area of the fracture surface by this propagation of the crack front is $w \times \Delta x$ and the energy required to extend the fracture surface is the work done to the gel, $\langle F \rangle \times \Delta x$. Therefore the fracture energy G is $(\langle F \rangle \times \Delta x) / (w \times \Delta x)$. This is identical to the quantity mentioned above.

In this study, we are interested in the fracture processes on the crack speed range from $V = 10\text{mm/s}$ to $V = 80\text{mm/s}$. On this V range, no remarkable roughening occurred on the fracture surfaces of the gels. Thus, we made no correction on $G(V)$ concerning with the roughness of fracture surfaces of the gels.

Viscoelastic measurement and swelling experiment— Viscoelastic measurement was carried out on cylinder-shaped gels (20mm diameter and 10mm height) in compressing mode with a rheometer (REO-GEL, UBM Co.). The range of oscillatory frequency f was from 0.1Hz to 80Hz. The sample of A7.5B4 showed weak viscoelasticity on the frequency range: at $f=0.01\text{Hz}$, $\tan \delta \approx 0.02$; at $f=50\text{Hz}$, $\tan \delta \approx 0.05$; and at 80Hz , $\tan \delta \approx 0.1$. Other samples (A7.5B6 ~ A7.5B18) showed nearly elastic response on the frequency range: $\tan \delta$ of them was less than 0.05 and the real part of the complex modulus E' was almost constant on the frequency range. We may regard the mechanical responses of the samples (including A7.5B4) as primarily elastic.

The equilibrium swelling ratio α was measured on disk-shaped gels. The diameter of the disk-shaped gels in preparation, d_0 , was 25 mm and the thickness of them was 1mm. The gels were immersed in distilled water (25 °C) for a

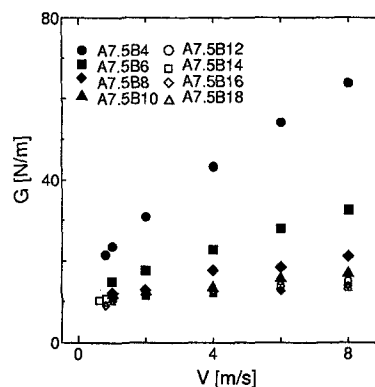


Fig.2: A plot of G as a function of V . $G(V)$ linearly depends on V . For high C_{BIS} samples (A7.5B12 ~ A7.5B18) the data points almost collapse on the scale of this plot.

week to reach the swelling equilibrium, and diameters of the swollen samples d_{eq} was measured with a pair of calipers. The swelling ratio α was determined by the relation $\alpha = (d_{eq}/d_0)^3$.

3. RESULTS

fracture energy— Figure 2 is a plot of the fracture energy G as a function of the crack speed V . The order of $G(V)$ is several hundred times as large as that of the surface tension of water (about 0.072 N/m at 25°C [5]). We can see the following behavior in Fig. 2:

- $G(V)$ for each sample linearly depends on V .
- For low C_{BIS} samples (\sim A7.5B10), G at a given value of V decreases with increasing C_{BIS} .

These results are consistent with our previous study [2, 3], and indicate that *the dissipative effects dominate over the effects of the breakage of polymer chains in $G(V)$* . An important result in this study is:

- For high C_{BIS} samples, $G(V)$ becomes insensitive to C_{BIS} .

Figure 3 is a plot of dG/dV (determined by the least-square fitting of the data in Fig. 2) as a function of C_{BIS} . Figure 3 clearly shows a crossover of C_{BIS} dependence of $G(V)$, which occurs around $C_{BIS}=9$.

mechanical and swelling behavior — Figure 5 shows C_{BIS} dependence of the Young's modulus E (we regard E equal to the real part of the complex modulus E' at $f=10$ Hz). At low values of C_{BIS} , E is proportional to C_{BIS} . At large values of C_{BIS} , the slope of the $E - C_{BIS}$ relation drops down. The crossover of C_{BIS} dependence of E occurs around $C_{BIS}=12$. Figure 6 is a plot of α versus C_{BIS} . Again we can find out a crossover around $C_{BIS}=8$.

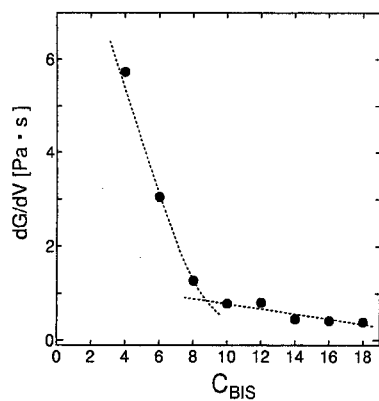


Fig.3: Dependence dG/dV on C_{BIS} . The dependence drastically changes around $C_{BIS}=9$.

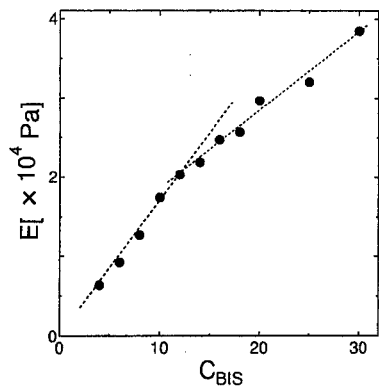


Fig.4: A plot of E versus C_{BIS} . The slope of $E - C_{BIS}$ relation drops down around $C_{BIS}=12$.

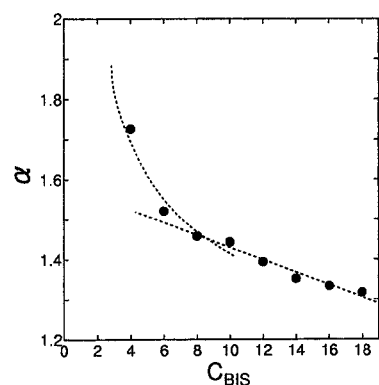


Fig.5: A plot of α versus C_{BIS} . The C_{BIS} dependence of α drastically changes around $C_{BIS}=8$.

4. DISCUSSION

In this study we investigate effects of preparing cross-linker concentration C_{BIS} on mechanical, swelling and fracture behavior of acrylamide gels. These three quantities qualitatively change on a narrow range of C_{BIS} . This implies that a qualitative change occurs in the network structures of the gels on the range of C_{BIS} .

Furukawa reported the following result on a crossover of swelling behavior of the acrylamide gels [4]: for the gels polymerized at low monomer and/or low cross-linker concentrations, the equilibrium swelling ratio is large and sensitive to slightly changes of the concentrations; on the other hand, for the gels polymerized at high monomer and/or high cross-linker concentrations, the equilibrium swelling ratio is small and insensitive to the changes of the concentrations. He referred the former type of gels as Gel I and the latter type of the gels as Gel II, and proposed the following interpretation: the gels of Gel I-type inherit the fractals at the gelation point and are rich with defects of network structure such as dangling chains; the gels of Gel II-type contain many *unbonded crossing points* as shown Fig. 6(b), which play the similar role with the chemical cross-link points against deformations just like the entanglements in polymer melts.

Based on Furukawa's study, we may construct the following picture about effect of C_{BIS} on the network structure of the gels used in this study.

There are many dangling chains in the network structures of the gels prepared at low values of C_{BIS} . Slightly increases in C_{BIS} alter the network structures of the gels through the following two processes: (i) The number of the chemical cross-link points increases, and (ii) a portion of the dangling chains changes into the sub-chains, producing the unbonded crossing points as shown in Fig. 6. On the other hand, for the gels prepared at sufficiently large values of C_{BIS} , the dangling chains are exhausted. Slightly increases in C_{BIS} alter the network structures of the large C_{BIS} gels only through the process (i).

The crossover in the $E-C_{BIS}$ relation can be interpreted based on the above observation because both the chemical cross-link points and the unbonded crossing points are relevant to E : below the crossover value of C_{BIS} both the processes (i) and (ii) are effective, and above it the process (ii) becomes ineffective and the slope of $E-C_{BIS}$ drops down. Similar interpretation is possible for the crossover in the swelling behavior in Fig. 6 because the swelling ratio reflects elasticity of the gels against osmotic driving force that tends to expand them.

As mentioned in the section 3, dissipation is the dominant effect in $G(V)$. The dangling chains should be responsible for the dissipative component in $G(V)$. Our interpretation for the crossover in $G(V)$ is as follows: below the crossover, where $G(V)$ is heightened due to the dangling chains, $G(V)$ and dG/dV sensitively

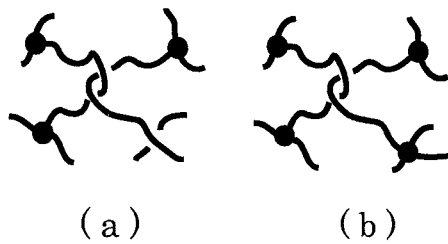


Fig.6: A long dangling chain (a) and a kind of topological constraint (unbonded crossing points, (b)). The unbonded crossing points would work as cross-link points against deformations.

decrease with increasing C_{BIS} because the number of the dangling chains decreases with increasing C_{BIS} . Above the crossover $G(V)$ and dG/dV become insensitive to C_{BIS} because the dangling chains are exhausted.

In summary we investigated the dependence of preparing cross-linker concentration on $G(V)$ of acrylamide gel, and compared it with mechanical and swelling behavior. On a narrow range of the cross-linker concentration C_{BIS} , crossovers were found in the swelling, mechanical and fracture behavior of the gel. A reasonable mechanism for the crossovers is the change in network topology of gels, i.e., the number of dangling chains.

References

- [1] A. J. Kinloch and R. J. Young, *Fracture Behavior of Polymers*, Elsevier, London and New York, 1983.
- [2] Y. Tanaka, K. Fukao and Y. Miyamoto, *Eur. Phys. J. E*, **3**,395-401(2000).
- [3] Y. Tanaka, K. Fukao and Y. Miyamoto, *Transactions of the Material Research Society of Japan*, **26**[2], 677-681(2001).
- [4] H. Furukawa, *Journal of Molecular Structure*, **554**, 11-19(2000).
- [5] *CRC Handbook of Chemistry and Physics*, ed. R.C.Weast, Chemical Rubber Company, 1999.

(Received December 20, 2002; Accepted March 24, 2003)