Tear Force of Physically Crosslinked Poly(vinyl alcohol) Gels with Different Submicrometer-Scale Network Structures

Taegu Noh, Yujiro Bando, Kensuke Ota, Saori Sasaki, Atsushi Suzuki

Department of Materials Science and Research Institute of Environment and Information Sciences, Yokohama National University, 79-7 Tokiwadai, Hodogaya-ku, Yokohama 240–8501, Japan
Correspondence to: A. Suzuki (E-mail: asuzuki@ynu.ac.jp)

ABSTRACT: Poly(vinyl alcohol) (PVA) gels can be easily prepared by either the freeze-thawing (FT gel) method or by the cast-drying (CD gel) method. Although the resulting nanostructured networks of the FT and CD gels are similar, their physical properties are quite different; while CD gels are transparent and elastic, FT gels are opaque and less elastic. Moreover, the tear energy of the FT gels is much greater than that of the CD gels, which is a direct result of micrometer-scale differences in their network structures. In order to control the distribution of microcrystallites on nano- and micrometer scales, FT gels were prepared from PVA solutions with different water contents. As a result, the gel gradually became more transparent as the initial water content was decreased; and accordingly, the tear energy decreased. Tear resistance was improved in the case of FT gels by repeating the number of FT cycles, whereas with CD gels, this was achieved by increasing the gelation temperature. These results indicate that the microscopic network structures are characterized by a micrometer-scale bundled-polymer (fibril), which determines the tear energy of FT gels. Simple methods to control the fibril network structure of FT gels using a unidirectional freezing method are presented herein, with the swelling and mechanical properties of modified FT gels discussed in terms of their multiple-scale network structures. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41356.

INTRODUCTION

The low toxicity, excellent mechanical strength, and high biocompatibility of physically crosslinked poly(vinyl alcohol) gels (physical PVA gels) makes them ideally suited for use as a biomaterial; and as such, there have been numerous studies into their practical applications across a variety of fields and into a variety of methods for their preparation.[1,2] Among these methods, the preparation of physical PVA gels by repeated freeze-thawing (FT gel) has been extensively studied for practical application in the healthcare and medical fields.[3,4] More recently, a simple method to prepare PVA gel by cast-drying has also been developed (CD gel).[5] In order to better understand the network structure produced by these methods on multiple-scales, physical PVA gels have been subjected to scattering and thermal measurement experiments[6–12] using X-ray diffraction (XRD), Fourier-transform infrared, and differential scanning calorimetry (DSC) techniques. As a result of XRD measurement, CD gel is known to consist of a swollen amorphous network of PVA that is physically crosslinked by microcrystallites, and is therefore similar to FT gel. From the literature,[2,11] there is little difference between the CD and FT gels in terms of the

average size of microcrystallites, D, and average distance between microcrystallites, L. Although the nano-scale network structures of the FT and CD gels are similar, the CD gels are transparent and elastic in nature, whereas the FT gels are opaque and less elastic. The most plausible reason for these differences is that the larger-scale distribution of microcrystallites, that is, from sub- to micro-micrometer order, differs between the two materials.[13]

It should be noted, however, that these observations of the minute structures were mostly obtained from dried or half-dried gels.[5,8] This has been the case because it is difficult to analyze the network structures of fully-swollen hydrogels when their water content, w, is high, as in the case of CD and FT gels (where $w > 80\%$ of the total weight). More recent experiments,[14] conducted by adding water incrementally to a CD film, have revealed that the magnitude correlation of D and L between samples is not affected by w; and thus, the network structures of the swollen gels can be qualitatively evaluated from the D and L of in their dried or half-dried state. Moreover, it was confirmed that the insights gained into the network structures by scattering measurements correlate well with the gel's

macroscopic properties, such as the swelling behavior of PVA gels. This can be explained by the fact that the swelling ratio is reflected by the average network structure, and so the macroscopic volume exaggerates microscopic conformations at a molecular level.[15] In other words, a small difference in the network structures can induce a change in the macroscopic volume. Therefore, both the nano- and micrometer-scale network structure can be inferred by simple measurements of the swelling and mechanical properties.

In this article, the mechanical behavior of physical PVA gels prepared by different methods (i.e., CD, FT and a CD-FT composite) is assessed through tear tests in water at room temperature. The swelling ratio and crystallinity are also measured, as these can easily have an influence over any differences observed in the network structures between samples. In addition, a novel preparation method for physical PVA gels is explored by controlling the polymer networks of FT gels via a unidirectional freezing method. A possible mechanism underlying the tear propagation behavior is then inferred in terms of the network structure, as characterized by the size, number, and distribution of microcrystallites, which have been reported by literature.[2,10,11,14]

EXPERIMENTAL

Sample Preparation

PVA powder, the raw material used in this study, was kindly supplied by Kuraray Co. and used without any further purification (Catalogue number: PVA117). Its average degree of polymerization was 1700, and the average degree of hydrolysis was between 98 and 99 mol %. The powder (PVA117) was mixed with deionized and distilled water (Milli-Q water) at a concentration of 15 wt % and dissolved with stirring at a temperature $> 90°C$ for more than 2 h. The resulting PVA pre-gel solution (15.0 g) was then decanted into an 85 mm diameter petri dish filled with polyethylene at room temperature.

Using this same PVA aqueous solution; FT, CD, and CD-FT composite gels were all prepared. To prepare the FT gels, the solution in the petri dish was covered with a lid and sealed with Parafilm to prevent evaporation of water, and then left in a freezer at around $-20°C$ for between 7 and 24 h. After this, it was placed in a temperature-controlled container at $4°C$, and subjected to four freeze-thaw cycles in total. The gels were then immersed in a large amount of pure water until they reached an equilibrium state, thus resulting in physical PVA gels (FT gels). To prepare the CD gels, the Petri dish solution was left uncovered to dry in air at room temperature ($\sim 25°C$) until the weight became almost constant. This dried gel though still contained some residual water [$w_{res} = 6 \pm 1$ wt %, evaluated by Thermo Gravimetry Analyzer (TGA4000; PerkinElmer)], and was subsequently soaked in a large amount of pure water to obtain a PVA cast gel, which is hereafter referred to as a CD gel. As for the CD-FT composite gels, FT gels were prepared after the PVA solution was dried to a final water content ranging from 85 wt % to w_{res}. This water content was controlled by leaving the 15 wt %-PVA solution ($w = 85$ wt %) in air at room temperature until the desired value was reached.

In the preparation of the FT gels, a unidirectional freezing method was utilized.[16–19] In this, the PVA solution was encapsulated in a mold consisting of a set of parallel acrylic plates separated by 40×50 mm silicone rubber spacers. These spacers were stamped from a 60×70 mm sheet 1 mm in thickness, and then adhered to an acrylic plate. The PVA solution was poured into this silicone rubber frame, with a second acrylic plate used to enclose the stamped space filled by PVA solution. The resulting mold was then connected to a position-controlled stepper motor and immersed in a 50 vol % ethanol water solution. The temperature of this solution was regulated at $-20°C$ with the longitudinal immersion of the mold controlled at a constant velocity of 0.01 mm·s^{-1}. Once the entire mold was submerged, it was held there for 1 h, and then removed and left at $4°C$ in air. This FT treatment was repeated four times. After gelation, the acrylic plates were carefully removed from the gel, thus forming a thin-plate anisotropic FT gel.

### Measurements of Swelling Ratio and Crystallinity

The as-prepared gels were immersed in large quantities of pure water at room temperature and left for over 48 h in order to reach their swelling equilibrium state. After the samples were removed from the water, any residual droplets of water on their surface were wiped off using Kimwipes, and the weight of the swollen sample, W_t, was measured at room temperature. After this measurement, the sample was dried at $60°C$ for more than 24 h, and the dried weight, W_d, was obtained. The swelling ratio, as defined by W_t/W_d, was then calculated.

The crystallinity was measured using a DSC (DSC8000; PerkinElmer), which was also used to determine the heat required to melt the microcrystallites in a PVA cast gel, ΔH. The measured temperature range was set at 25–250°C, and the heating rate was 10°C·min^{-1}. The crystallinity was calculated from the value of ΔH using literature data for the heat required to melt 100% crystalline PVA[20] ($\Delta H_{PVA} = 138.6$ J·g^{-1}).

Measurement of Tear Force and Tensile Strength

The tear force[21] was obtained by a trouser tear test in water. For this, the samples were first cut into a rectangular shape [0.5–0.6 mm (CD gel), 2.0 mm (FT gel) in thickness, 75 mm in length and 30 mm in width] and an initial slit (25 mm in length) was made in the center of one of the short sides, from which the tear propagated. The force generated during deformation was measured using a double leaf spring with four active strain gauges so as to maintain the accuracy of the measurements. In this test, the rate of separation of the grips holding the gel was held constant at 0.1 mm·s^{-1}. The tear energy, G, is defined as the fracture energy released per unit area of crack surface growth (J·m^{-2}), which was obtained here by dividing the tear force by the gel thickness.

For a tensile strength test, the gels in their equilibrium states were cut using a dumbbell cutter (JIS K-6251-8), and the dumbbell shaped test samples (0.5–0.6 mm in thickness, 50 mm in total length, the central parallel portion width and length being 8.5 mm and 16 mm, respectively) were used to obtain stress–strain ($\sigma-\varepsilon$) curves in air for their respective gels by a uniaxial loading test. The rate of elongational stretch between grips was 1.0 mm·s^{-1}, which was somewhat fast to prevent drying. The forces generated during deformation were measured using a tensile tester (INSTRON 5965; Instron Japan Co). Using
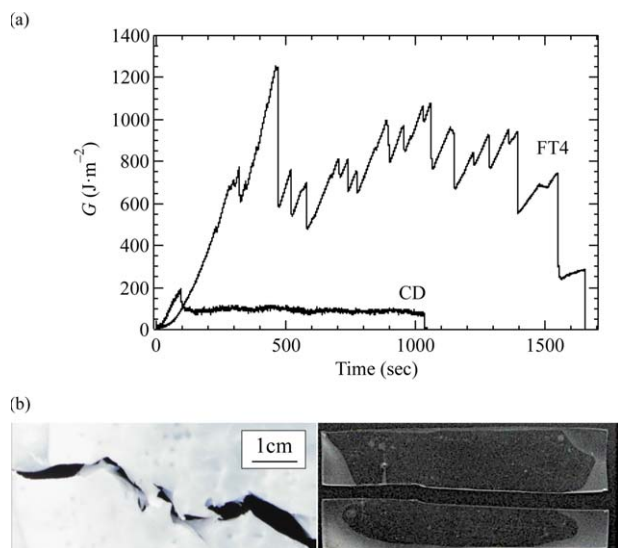
Figure 1. (a) Tear energy, G, of FT and CD gels during a tear test with a pulling velocity of $v = 0.1$ mm·s^{-1}. (b) Fractured surfaces of FT (left) and CD (right) gels. The data of CD gel is reproduced with permission from Figure 3(a) of Soft Matter, 8, 8129 (2012) (Copyright 1997 The Royal Society of Chemistry). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

a food dye, two markers were applied to the gel by hand in the gauge section (the central parallel portion). Images of the gel and markers were captured during the tests by a video camera and saved to a computer, from which the distance between the markers was analyzed to determine the strain. From the measured values of force and elongation, the nominal stress, σ, and strain, ε, were calculated; and from this, the breaking stress was obtained.

The initial tensile strength was evaluated using the data in the low strain region below about $\varepsilon = 0.2$. The data was plotted in log–log scale, and a solid line with slope $= 1$ was fitted to the linear region by the least-square plot.

RESULTS AND DISCUSSION

Tear Energy
Figure 1(a) shows the variation in G with time for both FT4 and CD gels. From this, it is evident that in the case of the CD gel, G exhibits a steady propagation after first peaking during the initial stage. This larger peak is attributed to the initial fracture energy required to initiate propagation in the vicinity of the slit end, a region in which the polymer network is reinforced due to the turbulence induced by cutting the slit. In the case of the FT gel, however, G exhibits a stick-slip behavior and the average G is much larger (roughly ten-times) than that of a CD gel in the flat region. Pictures of typically fractured gels by the tear tests are presented in Figure 1(b), in which a characteristic fracture pattern is observed. This appearance of stick-slip behavior in the fracture pattern of FT gel corresponds visually to the oscillatory tear curve. These results indicate that it is the microscopic network structure, as-characterized by the fibrils, that determines the tear energy of the FT gels. The appearance of stick-slip behavior and the large tear energy results from the

formation of a micrometer-scale network of fibril (bundled-polymer) and from the network inhomogeneity on a micrometer-scale.

Improved Tear Resistance
There are several factors that can affect the fracture force of hydrogels; such as the degree of crosslinkings, total concentration of polymer, and fracture velocity; all of which need to be examined to fully understand the tear mechanism. As shown in Figure 2(a), the G of CD gels increases with gelation temperature, T_{gel}, from 25 to 60°C. This suggests that a change in T_{gel} affects the network structures, especially with regards to the size, number, and distribution of microcrystallites, determined at gelation. According to the literature,[11] the growth of microcrystallites is enhanced by reducing the water content (i.e., evaporating bound water) of polymers with an increase in T_{gel}. In actuality, the present results shown in Figure 2(b) are consistent with the preliminary result;[11] in which W_t/W_d was reduced and the crystallinity increased with increasing T_{gel}. The
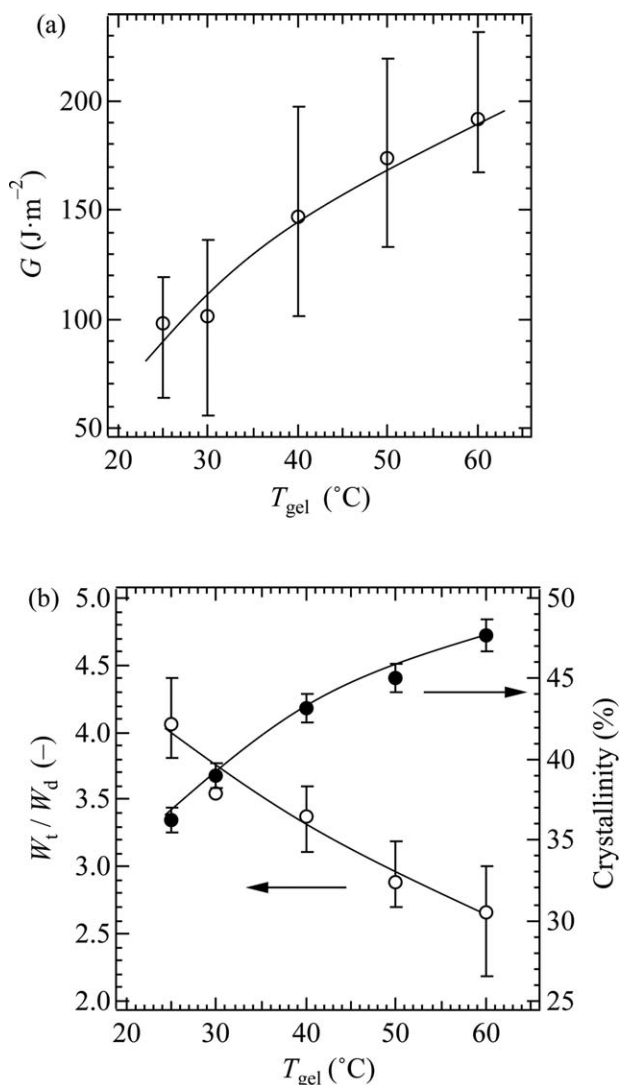
Figure 2. Effects of the drying temperature on (a) the tear energy, G, and (b) the swelling ratio, W_t/W_d and the crystallinity of CD gels.
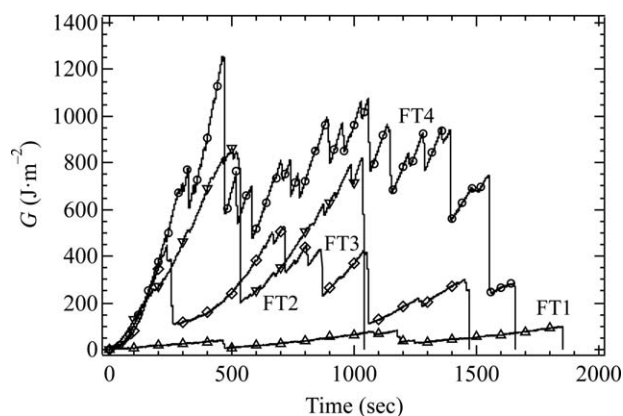
Figure 3. Effects of the number of FT cycles on the tear energy, G of FT gels. FTn denotes the gel prepared by the FT process was repeated n times for FTn gel.

measurements were conducted on three different samples except 30°C, which were prepared using the same method and at the same time. Furthermore, in the case of FT gels, the swelling ratio decreased and the crystallinity increased with an increasing number of repeated cycles and subsequent increase in G (Figure 3). This is also attributed to the increased formation of microcrystallites in the network by repeating the FT process.

The G of both CD and FT gels can therefore be increased by their respective simple treatments. The differences between CD and FT gels, in terms of the absolute value of G and the stick-slip behavior, indicate that the microscopic network structure characterized by fibrils determines the high tear-energy of FT gels.

Mixed Network Structures

The CD-FT composite gels were expected to incorporate aspects of the mixed network structures of CD and FT gels on multiple-scales, and thus exhibit unique swelling and mechanical properties. By decreasing w from 85 wt % to a selected w-value, microcrystallites are formed prior to the FT process, the extent of which being dependent on the value of w. As shown in Figure 4(a), the gel becomes transparent as the initial water content is reduced; and accordingly, the tear energy is also reduced [Figure 4(b)]. This is understandable given the decrease in W_t/W_d and increase in crystallinity that is associated with a reduction in w [Figure 4(c)]. These results therefore indicate that the network structure, characterized by micrometer-scale fibrils, can increase the tear energy. In other words, these fibrils can determine the tear energy of the FT gels.
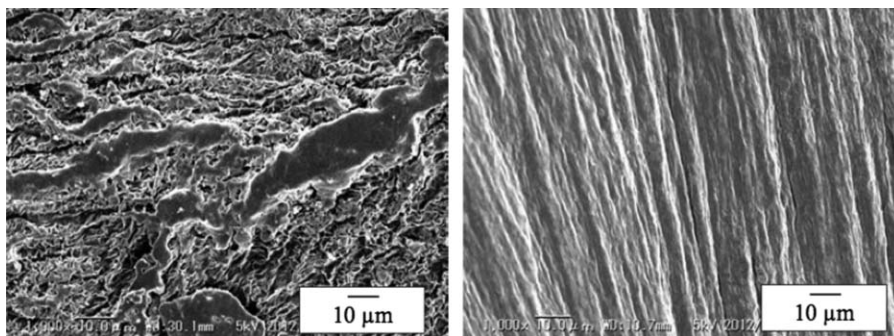
Anisotropic Gels

From the results presented thus far, the large tear resistance of physical PVA gels can be attributed to microscopic fibrils, and thus, much greater strength can conceivably be achieved by controlling their distribution. However, in order to significantly improve the mechanical properties, conventional methods may not be the most appropriate. Conventional FT and CD methods, for instance, are based on the phase separation induced by the natural solidification and vaporization of water. On the other hand, it is possible to achieve far superior gel properties by introducing an artificial process to control the polymer networks of FT and CD gels on multiple-scales.

To this end, a unidirectional freezing method was applied to control the fibril network structure of FT gels; this directional freezing providing a means of orientating the fibers along the freezing
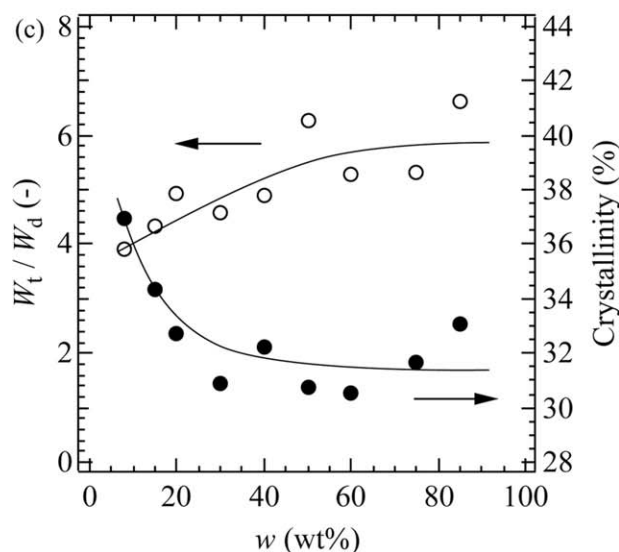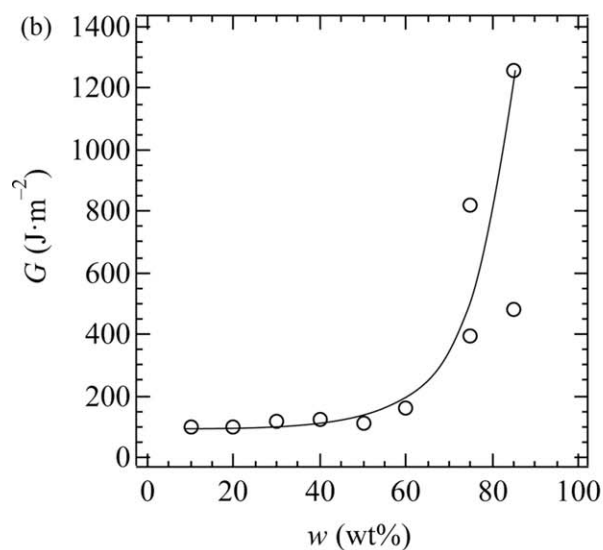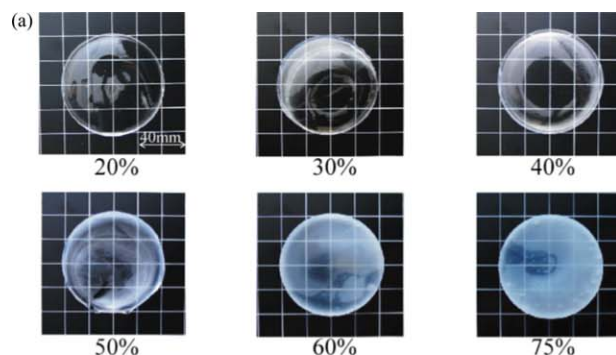
Figure 4. (a) Pictures of CD-FT composite gels prepared using the initial PVA solution with different water comtent, w wt %. (b) The tear energy, G and (c) the swelling ratio, W_t/W_d as a function of w. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5. SEM micrographs of a conventional FT gel (left) and an anisotropic dried FT gel (right).

direction. As a result, a micrometer-scale fibril network structure was successfully formed in FT gels, its anisotropic nature clearly evident in the SEM image of Figure 5. It should also be noted that the microscopic surface patterns reflect this micrometer-scale network, in which the fibrils are slightly connected to each other by the amorphous network. The crystallinity of the anisotropic gel, evaluated in the present study, was around 35%, which was almost the same as that of the conventional FT gel.[20] This result indicated that the different properties of both gels resulted from the different distribution of the microcrystallites introduced at gelation. It is therefore evident that this technique produces a microscopically aligned network structure that was not observed in those gels produced by a conventional single process. We are currently investigating the detailed structure of fibrils on nano- and micrometer-scales of the anisotropic gel in its swollen state, which will be presented elsewhere.

The tear energy of these anisotropic gels was assessed by the same trouser tear test in water, again using a rectangular sample with an initial slit. However, the fracture was not observed to propagate orthogonally ($\perp$) to the aligned direction (//), but instead propagated along the //-direction from the edge of the slit. As a result of this, a uniaxial loading test was applied to this sample instead of a trouser tear test. Figure 6 shows the nominal stress–strain (σ–ε) curve of an anisotropic gel that was elongated along the //- and $\perp$-directions. The initial slope of this curve in the low ε-range, which corresponds to Young's modulus, E, was found to be 0.10 MPa along the //-direction and 0.095 MPa along the $\perp$-direction. These values are shown to be nearly unchanged between both elongation directions, suggesting that the resistance to uniaxial load may be isotropic. According to the literature,[8,9] any increment in the breaking stress and E of a CD gel during water exchange with drying will result in an increase in crystallinity. Thus, to understand the present results, it must be assumed that the initial tensile strength is determined not by the fibrils, but by the amorphous network. It should be noted that this isotropic response in the initial elongation is different from the reported results for an anisotropic gel, which was prepared by controlling the stress applied during the freeze-thaw process.[22,23] This can be attributed to the micrometer-scale differences in their network structures, as characterized by the fibrils. More specifically, both anisotropic gels consist of the amorphous network crosslinked by microcrystallites. The network of the present anisotropic gel is composed of dense and dilute regions of microcrystallites, and the dense region forms

bundled-polymer (fibril) aligned in one direction on a micrometer-scale. On the other hand, the reported anisotropic gel[22,23] is composed of amorphous regions crosslinked by microcrystallites and elongated macropores, that is, polymer region and pore regions, and the polymer region forms anisotropic structure. In response to a small uniaxial stress, the amorphous region deforms isotropically in the former gel, while the polymer region deforms anistropically in the latter gel.

It should be noted that overall shape of the σ–ε curve is similar to that of isotropic FT gels.[17,24] This is different from that of CD gels,[11,14] which shows the rubbery plateau region at the middle range of strain.

Mechanical Strengthening

By employing a unidirectional freezing method, a micrometer-scale fibril network structure can be formed in FT gels, the anisotropic nature of which leads to a higher mechanical performance along the fibril direction. As shown in Figure 7, the nominal breaking stress along the fibril was much greater than for a conventional FT gel, which is comparable to that of a CD gel. The measurements were conducted on two different samples for CD, four for FT gels, and two for anisotropic FT gels (// and $\perp$), which were prepared using the same method and at the same time. The nominal stress is
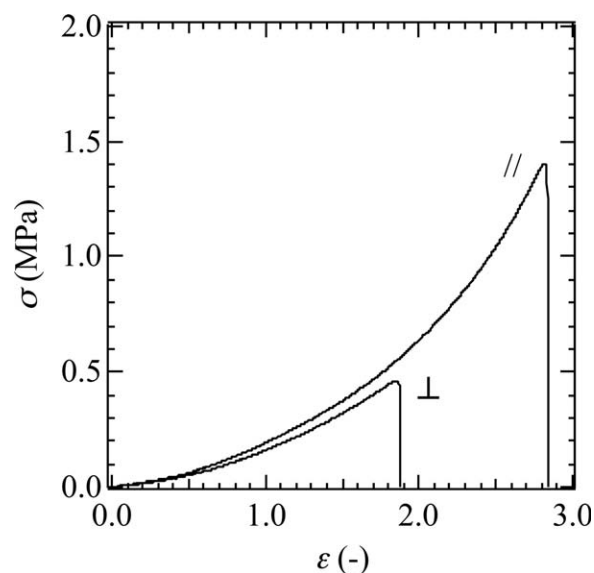
Figure 6. Nominal stress–strain (σ–ε) curve of anisotropic gel along the //- and $\perp$-directions on a uniaxial loading test.
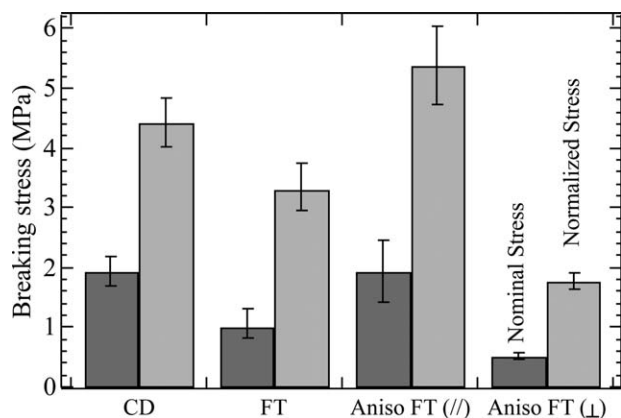
Figure 7. Breaking stress of PVA CD, FT, CD-FT composite, and anisotropic FT gels (abbreviated as Aniso FT). Nominal (left) and normalized (b) values.

defined as the ratio of force to the cross-sectional area of the swollen gel before elongation. In the case of a gel, although the cross-sectional area consists of a biphasic phase of solid (polymer) and fluid (water), the load during elongation is supported only by the polymer. Since the interstitial fluid has no influence on the tensile strength, the nominal stress is not suitable for comparing the strength of gels with different swelling ratios. The number of polymer chains per unit cross-sectional area of the swollen gel depends on W_t/W_d; the larger the W_t/W_d increases, the smaller the polymer number per nominal area becomes. To correct for the effect of swelling ratio on the elongation force, the nominal stress was divided by $(W_d/W_t)^{2/3}$, thus giving a normalized stress. This can be used an approximate measure of the tensile strength of a gel, thereby demonstrating that the normalized breaking stress along the //–direction is much larger than in other direction. In particular, the stress along the ⊥–direction was less than half as much, though it was nevertheless comparable to the nominal stress of a CD gel. To further explore the potential of this strengthening mechanism, the authors are currently developing a lamination method[13] and hybrid techniques[25] incorporating FT and CD gels, which shall be discussed in future publication.

CONCLUSION

Physical PVA gels in the form of CD, FT, and CD-FT composite gels were prepared by conventional methods and evaluated by tear energy measurement in water. In the case of CD gels, it was found that there is a decrease in the swelling ratio and an increase in tear energy with increasing T_{gel}. A similar effect was also apparent with increasing the number of repeated free-thaw cycles in preparation of the FT gels.

A unidirectional freezing method was applied to the preparation of physically crosslinked PVA gels, by which an anisotropic micrometer-scale fibril network was formed in FT gels. This anisotropic network structure was demonstrated to enhance the mechanical performance along the fibril direction, thereby confirming the viability of this method in producing a microscopically aligned network structure that have not been observed in gels produced by conventional single processes.

REFERENCES

1. Alves, M. H., Jensen, B. E., Smith, A. A., Zelikin, A. N. *Macromol. Biosci.* **2011**, *11*, 1293.

2. Hassan, C. M.; Peppas, N. A. *Adv. Polym. Sci.* **2000**, *153*, 37.

3. Peppas, N. A. *Makromol. Chem.* **1975**, *176*, 3433.

4. Tamura, K.; Ike, O.; Hitomi, S.; Isobe, J.; Shimizu, Y.; Nambu, M. *ASAIO Trans.* **1986**, *32*, 605.

5. Otsuka, E.; Suzuki, A. *J. Appl. Polym. Sci.* **2009**, *114*, 10.

6. Tadokoro, H.; Seki S.; Nitta, I. *Bull. Chem. Soc. Jpn.* **1955**, *28*, 559.

7. Watase, M.; Nishinari, K. *J. Polym. Sci., Part B: Polym. Phys. Ed.* **1985**, *23*, 1803.

8. Otsuka, E.; Suzuki, A. *Prog. Colloid. Polym. Sci.* **2009**, *136*, 121.

9. Otsuka, E.; Sasaki, S.; Koizumi, K.; Hirashima, Y.; Suzuki, A. *Soft. Matter.* **2010**, *6*, 6155.

10. Sasaki, S.; Otsuka, E.; Hirashima, Y.; Suzuki, A. *J. Appl. Polym. Sci.* **2012**, *136*, 233.

11. Otsuka, E.; Komiya, S.; Sasaki, S.; Xing, J.; Bando, Y.; Hirashima, Y.; Sugiyama, M.; Suzuki, A. *Soft Matter* **2012**, *8*, 8129.

12. Sasaki, S.; Suzuki, A. *React. Func. Polym.* **2013**, *73*, 878.

13. Murakami, T.; Yarimitsu, S; Nakashima, K.; Yamaguchi, T.; Sawae, Y.; Sakai, N.; Suzuki, A. *Proc IMechE Part J: J. Eng. Tribo.* **2014**, doi: 10.1177/1350650114530273.

14. Otsuka, E.; Sugiyama, M.; Suzuki, A. *J. Phys.: Conf. Ser.* **2010**, *247*, 012043.

15. Tanaka, T. *Sci. Am.* **1981**, *244*, 124.

16. Tong, H. M.; Noda I.; Gryte, C. C. *Colloid Polym. Sci.* **1984**, *262*, 589.

17. Yokoyama, F.; Masada, I.; Shimamura, K.; Ikawa, T.; Monobe, K. *Coll. Polym. Sci.* **1986**, *264*, 595.

18. Zhang, L.; Zhao, J.; Zhu, J.; Wang, H. 2012 *Soft Matter* **2012**, *8*, 10439.

19. Zhang, H.; Hussain, I.; Brust, M.; Butler, M. F.; Rannard S. P.; Cooper, A. I. *Nat. Mater.* **2005**, *4*, 787.

20. Hassan, C. M.; Peppas, N. A. *Macromolecules*, **2000**, *33*, 2472.

21. Tanaka, Y.; Abe, H.; Kurokawa, T.; Furukawa, H.: Gong, J. P. *Macromolecules* **2009**, *42*, 5425.

22. Millon, L. E.; Mohammadi, H.; Wan, W. K. *J. Biomed. Mater. Res. Part B: Appl. Biomater.* **2006**, *79*, 305.

23. Millon, L. E.; Nieh, M.-P.; Hutter, J. L.; Wan, W. K. *Macromolecules* **2007**, *40*, 3655.

24. Hyon, S. H.; Cha, W. I.; Ikada, Y. *Polym. Bull.* **1989**, *22*, 119.

25. Suzuki, A.; Murakami, T. *Encyclopedia of Biocolloid and Biointerface Science*, submitted.