Ultrahigh Ductile Gels Having Inter-Crosslinking Network (ICN) Structure*

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Gels have unique properties such as low frictional properties, permeability and biocompatibility due to their high water content. In the last decade, several high-strength gels have been developed, which are promising for extending the application of gels as industrial materials. Previously we proposed novel ultrahigh ductile gels by defining inter-crosslinking network (ICN) structure. In this study, the mechanical properties of ICN gel was studied by experiments and theoretical estimations, and the mesh size of the internal network structure were determined. It is found that the Young's modulus of ICN gels calculated by experiments well matches with the theoretical estimations. The appropriate ICN gels achieves more than 61% increase in the ductility in comparison with normal poly(*N,N*-dimethylacrylamide) (PDMAAm) gels, by introducing the ICN structure. For the ICN gels, the density of chains calculated from the mesh-size is well consistent with the other densities calculated from the modulus and the water content, in comparison with the PDMAAm gels. [DOI: 10.1380/ejsnt.2012.346]

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I. INTRODUCTION

Gels have three-dimensional network structures of macromolecules including solvent, and by virtue of their high water content they have low friction properties, permeability, and biocompatibility. These are promising as a next generation of industrial materials, especially advanced to medical applications. However, breaking stress in compression of usual gels is 0.1-0.4 MPa, which is quite low in comparison with the other hard materials, such as metal, ceramics, and plastics. The weak mechanical strength of gels had been a serious problem to use gels as industrial materials. This is why in recent years many trials were made to invent high-strength gels. In these trials, to develop epoch-making internal structures were important, such as Topological Gel, Nanocomposite Hydrogels, Double-Network Hydrogels, Tetra-PEG Gels, High-water-content mouldable hydrogels [1-8]. Especially, the Double-Network gels [3] achieves 30 MPa of breaking stress in compression test at the maximum, which is the best record in the world. Since these rein-

forced gels could make a breakthrough for problems of weakness of gels, the gels attract much attention as new materials, and some trials have been conducted for an application as biomedical materials to artificial joint. These reinforced gels could achieve the high strength owing to their characteristic three-dimensional network structure of macromolecules. One of the most interesting points of gels research is how we control the mechanics of gels by the network structure.

In our previous research, Inter Cross-linking Network (ICN) structure was proposed as a first time to achieve novel gels having ultrahigh ductility [9, 10]. Figure 1 shows the comparison of the internal structure of the ICN gel and other gels. In the case of Simple gels and Composite gels, the polymers have cross-linking points usually between the same types of polymers, and scarcely between the different types of polymers. The composite gel is sometimes categorized into an interpenetrated network. While, in the case of ICN gels, the intercross-linkers do not connect the same types of polymers, but connect the different types of polymers. Since the interaction between the same polymers is loose, the ICN network can deform largely in tensile test as shown in Fig. 1(d). This can be the reason for the properties of ultrahigh ductility [10].

In this study, mechanical properties of ICN gels were precisely examined by experimentally and theoretically. Experimental Young's Modulus of the ICN gels E_t were

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FIG. 1: Comparison of the internal structure of the ICN gel and the other gels. (a) shows a simple gel, which has single network structure. (b) shows a composite gel, which has crosslinking structure only between the same types of polymers. (c) shows the ICN gel which has crosslinking structure only between the different types of the polymer. (d) shows the schematic of the stretched inner structure of the ICN gel in tensile test.

determined by the stress-strain curve in tensile test and the theoretical Young's Modulus E_w were calculated by the equation of ideal rubber elasticity. By comparing both E_t and E_w , internal structure of the ICN gels were considered. Further, a characteristic length of internal structure, i.e. the mesh size of the ICN gels was also determined by scanning microscopic light scattering (SMILS), which is a dynamic light scattering system specialized for analyzing the microscopic structure in gels [11]. Three types of the density of elastically effective chains, ν_s , ν_w , and ν_t were calculated from the size of internal structure, the water content and the Young's modulus of tensile test. By comparing the three densities, the relation between the network structure and mechanical properties of the gels has been discussed.

II. EXPERIMENTAL

A. Synthesis of the ICN gels

Powder of the Hydroxypropyl cellulose (HPC, Wako Pure Chemical Industries Ltd., Japan) and α -keto (Wako Pure Chemical Industries Ltd., Japan) was added to liquid *N,N*-dimethylacrylamide (DMAAm, TOKYO CHEMICAL INDUSTRY CO., LTD., Japan) and stirred till the HPC was solved. Here, HPC is monomer, α -keto is photo initiator, DMAAm is monomer and also solvent. 2-(2-Methacryloyloxyethyl)ethyl isocyanate (Karenz MOI-EG, Showa Denko K. K.) as an intercross-linker was added and stirred for one hour to be reacted with the HPC. Then a little amount of water was added to stop the reaction of the Karenz MOI-EG and stirred for 30 minutes to be reacted with residual. The concentration of HPC was 0.5 mol% to DMAAm, and that of α -keto was 0.1 mol%. The molecular weight of HPC and the concentration of Karenz MOI-EG were controlled in order to vary the internal structure of ICN gels. The precise information is shown in Table I and our previous paper [10].

The substitutional ratio means how many Karenz MOI-EG molecules exist for one repeating unit (pyranose ring) of HPC. When a Karenz MOI-EG exists for a pyranose ring, the substitutional ratio is 100%. The pregel solution was poured into the mold that sandwiched the silicone spacer of 1 mm thickness between two pieces of glass plates, and was irradiated by UV lamp (the peak wavelength is 365 nm) for about 9 hours, then the gels were prepared. After the polymerization, the gels were soaked in a large quantity of pure water more than 48 hours to be fully swollen. The viscosity of HPC is related to the molecular weight of the HPC.

B. Tensile test of the ICN gels

The tensile test was performed to measure stress-strain relation by the same method as our previous study [10]. The gels were punched out in the shape of dumbbell specimen (JIS K6251 Dumb-bell test pieces No. 8). The thickness of the sample was fixed at 3 mm, the distance between the marked points was fixed at 16 mm. The mechanical testing instrument STA-1150 (ORIENTEC) was used for the tensile test, and the test was performed at 100 mm/min of crosshead speed. The tensile test was done in room temperature.

C. Measurement by Scanning Microscopic Light Scattering (SMILS)

The SMILS is the dynamic light scattering system specialized for gels or inhomogeneous solutions, as described in Ref. [11]. The ICN gels were observed by the SMILS with 532 nm laser beam. The distribution of the internal size, such as, mesh size of ICN gels can be calculated by the SMILS.

III. RESULTS AND DISCUSSIONS

A. Mechanical properties of ICN gels

The inset in Fig. 2 shows the stress-strain curves of the ICN gels in the tensile test. The numbers correspond to the sample numbers of Table I. It is found that the substitutional ratio clearly effects on the stress-strain curves. When the substitutional ratio is higher, the maximum breaking stress is higher, and the maximum strain is lower. When the substitutional ratio is lower, the maximum breaking stress is lower, and the maximum strain is higher. It implies that the relationship between the maximum stress and the maximum strain is trade-off. The precise value is shown in Table I. Sample (5) shows the largest maximum strain of 6.38 in all of the samples, which is 161% improved from the normal poly(DMAAm) (PDMAAm) gel. The water content of the ICN gels were well over 90%, ranging from about 91.5 to 97.6%.

Figure 2 shows the close up the stress-strain curves, whose region is indicated by the red rectangle in the inset of Fig. 2. The liner relationship between tensile stress σ and strain ε in this region are formulated with $\sigma = E_t \varepsilon$.

TABLE I: Experimental condition of ICN gels, maximum strain and water content.

Sample Number	Viscosity of HPC ^a (mP·s)	Ratio of MBAA ^b (mol%)	Substitutional ratio ^c (%)	Maximum strain	Water content (wt%)
PDMAAm Gel	No HPC	0.05	N/A	3.58	94.5
ICN Gel (1)	2.0-2.9	0	100	1.86	91.5
ICN Gel (2)	2.0-2.9	0	30	3.24	94.7
ICN Gel (3)	1000-5000	0	100	1.84	91.9
ICN Gel (4)	1000-5000	0	30	5.11	96.6
ICN Gel (5)	1000-5000	0	10	6.38	97.6

^aViscosity of HPC for 1wt% aqueous solution at 25°C. The higher viscosity corresponds to the higher molecular weight.

^bMolar ratio of MBAA to DMAAm.

^cThe substitutional ratio means how many Karenz MOI-EG molecules exist for one repeating unit (pyranose ring) of the HPC. When a Karenz MOI-EG exists for a pyranose ring, the substitutional ratio is 100%.

FIG. 2: Stress-Strain curve of the ICN gels. The inset is the whole curve, and the red rectangular is close up at the range of strain 0 to 1, where the straight lines are fitted to the S-S curves to calculate the Young's modulus E_t .

TABLE II: Comparison of Young's Modulus, E_t and E_w , of each samples.

Code of the sample	Viscosity of HPC (mP·s)	Substitutional ratio (%)	E_t (kPa)	E_w (kPa)
PDMAAm Gel	No HPC	N/A	13.52	2.06
ICN Gel (1)	2.0-2.9	100	33.05	31.36
ICN Gel (2)	2.0-2.9	30	10.95	5.89
ICN Gel (3)	1000-5000	100	41.28	30.3
ICN Gel (4)	1000-5000	30	4.86	3.82
ICN Gel (5)	1000-5000	10	1.63	0.89

E_t is the Young's modulus of the tensile test that was calculated from the slope of Fig. 2. Differently, the Young's modulus can also be estimated theoretically from the density of elastically effective chains ν_w , which is determined from the water content, based on the formula of entropic elasticity in the case of a perfect 4-functional network under the affine network assumption [12, 13], $E_w = 3\nu_w k_B T$, where k_B is the Boltzmann constant and T is the absolute

FIG. 3: The comparison between E_t and E_w , depending on the substitutional ratio related to the crosslinking density.

temperature. The ν_w is the density of elastically effective chains determined by the number of inter-crosslinking point divided by volume of gels after fully swelling. It is noted that ν_w of fully (equilibrium) swollen gels is sometimes distinguished from ν_w of as-prepared gels, if we consider both the states of preparation (ϕ_0) and measurement (ϕ). For example, $\nu = \nu'(\phi_0/\phi)^{2/3}$, where ν and ν' are the densities of the elastically effective chains in swollen and as-prepared states for θ -solvent [13]. Here we treat only ν without due consideration for ν' , because all the measurement were done for fully swollen gels. Table II shows both the E_t and E_w of all the gels for comparison. It is noted that sample (5) indicated 1.63 kPa, which is the smallest E_t . This E_t decreased by 12% in comparison with the normal PDMAAm gels.

Figure 3 shows the change in the E_t and E_w depending on the substitutional ratio. First of all, we see that E_t and E_w are well matched. It implies that the Young's modulus of the ICN gels is well controlled by the inter-crosslinking density. For the same viscosity of the HPC, it is found that the E_t and E_w increases as the substitutional ratio increases. Since the increase of the substitutional ratio means the increase of the inter-crosslinking point, this increasing behavior of the E_t is well understood by the

TABLE III: Mesh size determined by the SMILS and the three kinds of inter-crosslinking densities, ν_s , ν_w , and ν_t , calculated from the mesh size of the SMILS, the water content, and the Young's modulus of the tensile test.

Code of the sample	Mesh size 2ξ (nm)	ν_s ($1/m^3$)	ν_w ($1/m^3$)	ν_t ($1/m^3$)
PDMAAm Gel	8.08	1.90×10^{24}	1.66×10^{23}	1.08×10^{24}
ICN Gel (2)	13.10	4.45×10^{23}	5.01×10^{23}	8.73×10^{23}
ICN Gel (4)	16.40	2.27×10^{23}	3.19×10^{23}	3.87×10^{23}

formula of the entropic elasticity theory, $E_w = 3\nu_w k_B T$. Comparing E_t and E_w in detail, E_t is slightly larger than E_w for HPC1000~5000 in the high substitutional ratio. It implies that as the chain length of the HPC is larger, the entanglement among the polymer chains becomes so frequently that the entanglement possibly increases the apparent Young's modulus. By the way, we expect that the decrease of the inter-crosslinking point hopefully possibly causes the loose structure in the ICN gels as abovementioned. Namely, we expect that when the substitution ratio decreases, the stress concentration caused by the tensile test tends to be avoided due to its loose structure, which makes the gel deform largely. The experimental result well matches with our expectation.

B. Size of internal structure

The internal structure of the PDMAAm gel and the ICN gels (4) and (8) were measured by SMILS, and the characteristic mesh-size of network structure 2ξ was determined as shown in Table III. Also, the density of elastically effective chains ν_s is calculated from the 2ξ , as follows. If it is simply assumed that the structural unit in the ICN-gels is like a cube, the volume of the unit is calculated by $v = (2\xi)^3$. If ν_s corresponds to the density of the unit, ν_s is calculated by $\nu_s = (1/v)$. Table III shows this calculated ν_s and the ν_w calculated from the water content in the Section III.1. Further, the other ν_t is calculated from the Young's modulus of tensile test E_t , by the formula of the entropic elasticity theory, $\nu_t = E_t/(3k_B T)$, as shown in Table III.

Figure 4 shows the dependence of ν_w and ν_t on ν_s . It is noted that the ν_w and ν_t are calculated from the mechanical properties of gels, while the ν_s is calculated from the structure of gels. Thus Fig. 4 shows the relations between the structure and the mechanical properties. In Fig. 4, the straight line of $\nu_w = \nu_s$ and $\nu_t = \nu_s$ implies the correspondences between the structure and the properties, due to the homogeneous network structure in gels, as shown in the inset illustration of network structure (b) in Fig. 4. In comparison with the PDMAAm gels, the plot of the ICN gels is close to the line. On one hand, when the network structure has the entanglement as shown in the inset (a) in Fig. 4, the entanglement prevents the swelling of gels and increases the modulus of gels, and thus the plot tends to be in the region of $\nu_w > \nu_s$ and $\nu_t > \nu_s$. On the other hand, when the network structure has many

FIG. 4: The densities of effective chains, ν_w (filled circle) and ν_t (filled triangle), calculated from the water content and the Young's modulus E_t , as functions of the other inter-crosslinking density, ν_s , calculated from the mesh size 2ξ .

dangling chains with no entanglement as shown in the inset (c) in Fig. 4, the mesh size observed by the SMILS tends to be smaller due to the narrower distance between the chains. It causes the increase of the ν_s . Here the dangling chains do no work on the increase of the modulus and cause the increase of the swelling, and thus the plot tends to be in the region of $\nu_t < \nu_s$ and $\nu_w < \nu_s$. As the plot of the DMAAm gels is in this region, it implies that the DMAAm gels has many dangling chains inside.

IV. CONCLUSIONS

We studied the mechanical properties and network structure of the ICN gels. The maximum strain of the ICN gels achieves 6.38, i.e. 61% higher than normal PDMAAm gels. The relationship between the increase of maximum strain and maximum stress is trade-off, which should be overcome to develop tough and ductile ICN gels in future. The decrease of the inter-crosslinking density provides the effective stress relaxation and large deformation in the ICN gels. The Young's modulus calculated from tensile test E_t well matches with that calculated from the water content E_w . The internal structure of ICN gels were observed by the SMILS. It implies that the ICN gels has more homogeneous and less dangling structure than the PDMAAm gels.

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