Ultrahigh Ductile Gels Developed by Inter Cross-linking Network (ICN)*

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Abstract
Gels have low frictional properties, permeability and biocompatibility due to 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. In this study, ultrahigh ductile gels are proposed by developing Inter Cross-linking Network (ICN), which is the novel internal structure of gels. The ICN gels can achieve more than 67.9% increase in the ductility in comparison with normal poly(N,N-dimethylacrylamide) gels, only by adding a little amount of fiber, hydroxypropyl cellulose, which is known as lyotropic crystalline polymer, while containing 97wt% water.

Key words: Gel, Inter Crosslinking Network, Ductility, Tensile Test, Water Content

1. 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. On the other hand, hard materials, such as metal, ceramics, and plastics, do not have such superior functions. However, breaking stress in compression of usual gels is 0.1-0.4MPa, which is quite low in comparison with the other hard materials. Due to such a low mechanical strength, it is difficult to apply usual gels to industrial materials. However, an epoch-making reinforcement method of the gels, such as Topological Gel, Nanocomposite Hydrogels, Double-Network Hydrogels, Tetra-PEG Gels, High-water-content mouldable hydrogels, has been devised in sequence since 2001(1-8). Especially, the Double-Network gels(3) could achieve 30MPa of breaking stress in compression test at the maximum, which is the best record in the world. Since these reinforced 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 order to extend further the application of the gels as industrial materials, here we focus on the development of novel gels having ultrahigh ductility. We propose a novel network structure as a first time in the world, which is named Inter Cross-linking Network (ICN) structure(9,10). We synthesize the ICN gels and analyze their mechanical and swelling properties. It is discussed that the effects of the addition of liquid crystalline polymer and cross-linker on the properties of the ICN gels.
2. Inter Crosslinking Network (ICN) structure

The Inter Crosslinking Network (ICN) is just introduced as a novel internal structure of the gels\(^9,10\). Figure 1 shows the comparison of the internal structure of the ICN gel and other gels. Simple gel (Figure 1(a)) has a network structure consisting of a single polymer. Composite gel (Figure 1(b)) is made by combining several kinds of polymer networks. In the composite gel, the polymers have cross-linking points usually between the same types of polymers, and scarcely between the different types of polymers. Thus the composite gel is sometimes categorized into an *interpenetrate network*. The ICN gel (Figure 1(c)) is made by combining several kinds of polymers with intercross-linkers. The intercross-linkers does not connect the same types of polymers, but connect the different types of polymers. Such a specific cross-linking network structure did not be defined before, as far as we know. Thus the ICN structure is a novel concept in the internal structure of the gel. Since in the ICN gel the interaction between the same polymers is loose, compared to the composite gel, the ICN network will deform largely in tensile test and the maximum of strain will increase, that is, ultrahigh ductility can be achieved.

![Figure 1](image1.png)

Figure 1. Comparison of the internal structure of the ICN gel and other gels. (a) shows Simple gel, which has single network structure. (b) shows Composite gel which has cross-linking structure made only between the same types of the polymer. (c) shows the ICN gel which has crosslinking structure made only between the different types of the polymer.

3. Design of the ICN gels

Figure 2 shows the chemical structure of the materials used in this study. Here, we synthesize the ICN gels from two kinds of polymer. \(N,N\)-dimethylacrylamide (DMAAm) is used as a monomer for polymerization of the one component of the two polymers. Single poly(DMAAm) gel is known as a flexible and ductile gel. Hydroxypropyl cellulose (HPC) is used for the other component of the two polymers. The HPC polymer is known as a lyotropic liquid crystalline polymer in aqueous solution. The HPC has rigid main-chain, which shows rod-like structure in water. Soft and flexible poly(DMAAm) chains cross-link to the rod-like HPC. Since the flexible polymer poly(DMAAm) links the hard rod HPC and makes a ICN gel, the ICN gel bears up under large pulling deformation, and possibly achieves ultrahigh ductility. We assume that in the ICN gel the HPC behaves like a frame timber and also behaves as a mobile framework during pulling deformation. That is, the rod-like HPC which exists across the poly(DMAAm) from another HPC can slip each other during the pulling deformation. This slip is easy to occur at a small concentration of the cross-linker since the fixed points are few. This thought is shown as Fig. 3.
In the preparation of sample ICN gels, DMAAm was also used as a solvent since DMAAm is in liquid state in room temperature. In order to cross-link the HPC and the DMAAm, a special crosslinker is used, that is, Karenz MOI-EG which has both double bond (methacryl group) and OH-reactive part (isocyanate group). When Karenz MOI-EG is mixed with HPC in solution, the hydroxyl group of HPC is attacked by the isocyanate group of Karenz MOI-EG and they are connected with the covalent bond between them. Then the modified HPC has the double bond and is able to react with DMAAm as a multi-functional cross-linker having rod-like shape. The $\alpha$-ketoglutaric acid ($\alpha$-keto) is added as a photo initiator in order to occur radical polymerization at the methacryl group of Karenz MOI-EG, which is connected to HPC in liquid DMAAm by UV irradiation. Then the gel is formed as drawn in Figure 1(c). Besides, $N,N'$-methylenebis-acrylamide (MBAA) is used for cross-linker among poly(DMAAm) to study the effect of the different chemical structures of cross-linkers, i.e., the MBAA and the modified HPC.

![Chemical structures of the materials used in the present study.](attachment:chemical_structures.png)

Figure 2. Chemical structures of the materials used in the present study.

![Schematic of inner structure of the ICN gels in tensile test.](attachment:schematic.png)

Figure 3. Schematic of inner structure of the ICN gels in tensile test.
4. Preparation of the ICN gels

Powder of the HPC (Wako Pure Chemical Industries Ltd., Japan) and α-keto (Wako Pure Chemical Industries Ltd., Japan) was added to liquid DMAAm (TOKYO CHEMICAL INDUSTRY CO., LTD., Japan) and stirred till the HPC was solved. The Karenz MOI-EG (Showa Denko K.K., Japan) 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 MBAA (Wako Pure Chemical Industries Ltd., Japan) and α-keto (Wako Pure Chemical Industries Ltd., Japan) were added and stirred. Then the mixed 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. Table 1 shows the composition of all the sample gels prepared in this study. The substitutional rate of Karenz MOI-EG 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 rate is 100%. 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.

5. Tensile test of the ICN gels

The tensile test was performed to measure stress-strain relation. 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 all the test was performed at 100 mm/min of crosshead speed. When we use the instrument STA-1150 (ORIENTEC), 5, 100, 500 mm/min can be chose as the crosshead speed. We chose 100 mm/min, since 5 mm/min took more than 100 min for a sample, while 500 mm/min is too fast to observe breaking of the gels. The measuring time is less than 5 min for 100 mm/min, thus, the evaporation of water from gels should not be the problem. The real image of the tensile test is shown in Fig. 4. The tensile test was done in room temperature.

<table>
<thead>
<tr>
<th>Code of the samples</th>
<th>Viscosity of HPC for 1 wt% aqueous solution at 25°C [mPa·s]</th>
<th>Substitutional rate of Karenz MOI-EG to HPC [%]</th>
<th>Ratio of MBAA to DMAAm [mol%]</th>
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<tr>
<td>Poly(DMAAm) Gel</td>
<td>No HPC</td>
<td>N/A</td>
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</tr>
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<td>(1)</td>
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<td>100</td>
<td>0.05</td>
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<tr>
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<td>2.0-2.9</td>
<td>30</td>
<td>0.05</td>
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<tr>
<td>(9)</td>
<td>1000-5000</td>
<td>10</td>
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Table 1. Composition of prepared gels.
Figure 5 shows the stress-strain curves of the ICN gels. Sample (9) is stretched the longest and its maximum strain is 6.65. This ICN gels can achieve 168% larger strain than normal poly(DMAAm) gel. However the relationship between the tensile stress and strain has trade-off problem, that is, the sample (9) shows the longest strain but the weakest. Here, Young modulus of gels is related to moisture content mostly, not related to the composition of molecules. The Young modulus of Sample (4), (8) and (9) is lower than Poly(DMAAm) gel, since Sample (4), (8) and (9) show extremely high water content as shown in Fig. 9.

Figure 6 shows the maximum strain of the various samples. Numbers of samples for each data are 3, the error bars show the maximum value and minimum value, which is the
same for Fig. 7 and 8. It is found that, when the substitutional rate of Karenz MOI-EG is the lower, or the viscosity of HPC is the higher, or the concentration of MBAA is the smaller, the maximum strain becomes the larger. Further, we confirm that the tensile test is possible even for the sample prepared without MBAA. It indicates that the rod-like HPC modified with Karenz MOI-EG can make DMAAm gel without MBAA, which is enough rigid for tensile test, and the Karenz MOI-EG works as the intercross-linker.

![Graph showing maximum strain at various composition.](image)

Figure 6. Maximum strain at various composition. (1) - (9) are the codes of the samples shown in Table 1.

Figure 7 shows maximum strain as functions of the concentration of cross-linking point. The concentration of cross-linking point is calculated by the following formula:

Concentration of cross-linking point\([M]\)  
\[\text{Concentration of cross-linking point} = \frac{\text{Number of cross-linking point} \ [\text{mol}]}{\text{Volume after swelling} \ [\text{L}].}\]

It is found that the maximum strain increases as the concentration of cross-linking point decreases. When the viscosity of HPC becomes higher, which is related to the higher molecular weight of the HPC, the maximum strain becomes larger.

Figure 8 shows the maximum stress as functions of the concentration of cross-linking point. The maximum stress increases with the increase of the cross-linking points. Besides, when the viscosity of HPC is higher, which is related to the higher molecular weight of the HPC, the maximum strain becomes larger. The large molecular weight corresponds to the length of the main chain of HPC. The number of the cross-linking point along the main chain of the HPC is just proportional to the length of the main chain. Thus, the ductility of gels is just related to the length of HPC that is viscosity of HPC.

These experimental results and ICN structure indicate that the ICN gels can disperse the stress concentration by relocating the network structure of molecules in the gels, such as the slipping of HPC. This relocation can be manipulated by controlling the molecular concentration. Such stress relaxation ideas is quite innovative as far as we know, since the DN gel can achieve high strength due to internal fracture of the network structure.
6. Water content of the ICN gels

The water content of the gel was measured by using Moisture Analyzers MS-70 (AND Co.). Figure 9 shows the water content of the various samples. Sample (9), which is stretched the longest and whose maximum strain is 6.65, has the highest water content of 97.6wt%. As the substitutional rate of Karenz MOI-EG decreases, or the viscosity of HPC increases, or the concentration of MBAA decreases, the water content increases. This tendency is the similar to the relation between the maximum strain and the concentration of cross-linking point (Figure 7). It implies that the chain length between the cross-linking points becomes longer, then the gel swells larger.

Figure 7. Maximum strain as functions of the concentration of crosslinking point.

Figure 8. Maximum stress as functions of the concentration of cross-linking point.
7. Conclusion

We designed and prepared the novel ductile ICN gels and measured their mechanical and swelling properties. It is possible to prepare the ductile ICN gels from the DMAAm monomer and the HPC polymer with Karenz MOI-EG as the intercross-linker even without the conventional cross-linker of MBAA. The maximum strain of the ICN gels achieves 6.65, where its water content is 97.6wt%. The ICN gels have 168% longer elongation than normal poly(DMAAm) gels. The maximum strain increases, as the substitutional rate of Karenz MOI-EG decreases, or the viscosity of the HPC increases, or the concentration of the MBAA decreases. That is, the ICN gels make the stress relaxation possible by manipulating the molecular structure.

Acknowledgments

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