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Interpenetrated polymer network (IPN) of gelatin (Glt) and sodium polyalginate (Alg) is studied to prepare Alg gel, which is expected to be more uniform than that prepared directly at high added salt (NaCl) concentrations, C_S. The mixed solution and IPNs are homogeneous at lower C_S. It was found that the mixed solution get phase separated around C_S =0.35M. The gels made from the phase separated solution were also investigated. The roughness of Alg gels prepared via IPN and directly at higher C_S is almost the same. It can be summarized that the phase separation was brought by higher C_S and it is not suitable to prepare uniform Alg gels with higher C_S. It was pointed out that the Alg gels prepared with lower C_S via IPN shows narrower elastic modulus distribution than the higher ones.

1. Introduction

The crosslinks in three-dimensional polymer network can be clarified into two categories. One is chemical crosslink formed by covalent bonds between polymer chains and the other is physical crosslink by coagulation of small parts of polymer chains due to ion complex formation, microcrystalline, and so on. Gel is a swollen state of three-dimensional polymer network containing solvents stabilized by thermodynamic interaction between polymer and solvent. Usually, the physical crosslink is weaker than the chemical crosslink. As a result the physical gel is also weaker than the chemical gel. However, the physical gels have reversibility in sol-gel transition at certain conditions. With such characteristics physical gels are widely used in foods, medical treatments, pharmacy, and etc.

In order to create new high performance materials, the research for multi component systems are carried out for polymeric materials.[1)2)] In the case for polymer networks, interpenetrated polymer networks (IPN), in which individual component polymer chains are connected with the same species by physical or chemical crosslinks, have been studied for expectation of better properties by interlocking of different polymer species.

When two polymers having different crosslinking mechanisms are employed for components of physically crosslinked IPN, it is expected that the crosslinking of components can be controlled independently. It was reported that polyvinyl alcohol (PVA)/sodium polyalginate (Alg) system with low Alg content composes IPN and the final structure does not depend on the gelation order of components.[3-7)] Nakamura[8)] studied gelatin (Glt)/Alg systems with a low added salt concentration C_S. It was reported that by removing the Glt from the IPN, more uniform Alg gel can be obtained than the gel prepared directly from Alg solution.

We attempted to study elastic properties of IPN of Glt/Alg system and Alg gel via IPN with high C_S to examine the effects of added salt and found that phase separation takes place for Glt/Alg at high C_S. In this study, phase diagram for Glt/Alg solutions with fixed C_{Glt} and C_{Alg} at a typical concentration used for IPN preparation with varying C_S is reported to examine the phase separation behavior of this system. The effect of phase separation on elastic property also examined for samples prepared with C_S=0.5M.

2. Experimental

2.1 Materials and sample preparation

Sodium poly alginate (Alg: weight average degree of polymerization 650; the ratio of β-D-mannuronate (M) and α-L-guluronate (G); M:G= 1:1.3) is purchased from Nakalai Tesque, Inc. Cooking gelatin is purchased from Morinaga & Co., Ltd. These polymers are used without further purification. Weighted amounts of the Alg and Glt are dissolved into deionized water with added salt, NaCl. Then the mixed solutions are prepared by simply mixing prescribed amount of two solutions and kept at 60℃ for 2 days. Intrinsic viscosity $[\eta]$ of the prepared Alg/Glt solutions are measured by the Ubbelohde viscometer at 25 ℃ to determine the degree of overlapping of polymer chains. Concentration C of components are determined by initial weight of samples and total weight of final samples. In this paper, the subscripts Alg and Glt are used for C and $[\eta]$ to specify the polymers.

2.2 Observation of phase separation and gelation

The well dissolved mixed solutions of Alg/Glt (C_{Alg}=0.5wt%, C_{Glt}=5wt%) with different C_S are transferred to test tubes and kept at 60℃ in the oven for 4 more hours. Then, the test tubes are put into a water bath. The initial temperature of water bath was 50℃. Then the temperature was decreased to 25℃ with 5℃ decrement to observe the changes in the test tube. At each temperature, observation was done after 10 minutes duration. Finally, the test tubes are put into refrigerator and kept at 4℃ for 4 hours. Then the test tubes are taken out to further observe the change in samples and to measure elasticity.

2.3 Preparation of IPN and gel samples

Glt-Semi-IPN (Glt gel containing Alg) was prepared from the mixed solution by cooling in refrigerator for 12 hours at 4℃. IPN was prepared from the Glt-Semi-IPN by soaking it in 1M $CaCl_2$ aqueous solution for 2 days, changing the $CaCl_2$ solution each day. The Alg gel was prepared from the IPN by keeping the IPN at 40℃ for 20 days in NaCl aqueous solution, changing the solvent for several times to fully dissolve and remove the Glt. Note that C_S was kept constant in these treatments. After above treatment, the Alg gel was removed from the solvent and kept at room temperature for about 4 hours before the measurements. The room temperature was kept at around 25 ℃.
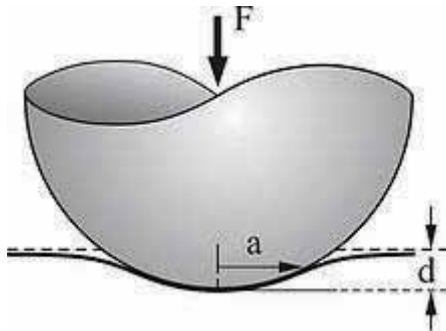
2.4 Elastic modulus measurement

Fig. 1 Schematic illustration of contact between a sphere and an elastic body.

Indentation method[9] is used to measure the elastic modulus of IPNs and gels. When an elastic sphere of radius R is indented into an elastic half-space to depth d, as shown in Figure 1, the applied force F is related to R and d by

$$F = \frac{4E^*R^{1/2}d^{3/2}}{3} \qquad (1)$$

Where E^* can be related to the elastic moduli E_1 and E_2 and the Poisson's ratio υ_1 and υ_2 of each body by

$$\frac{1}{E^*} = \frac{(1 - \nu_1^2)}{E_1} + \frac{(1 - \nu_2^2)}{E_2} \qquad (2)$$

Let the sphere be material 1 and be a rigid body, so that we can assume $E_1=\infty$. Then, by evaluating F and d, the elastic modulus of sample E_2, can be derived from equations (1) and (2).

Figure 2 shows our homemade simple elastic modulus meter. It is consisted of 4 parts: main pole, shaft, micrometer, and electronic balance to measure F. There is a valve on the top of the main pole to control the height of the shaft, on which the micrometer is fixed. The tip having a half spherical end can go up and down by turning the valve on the micrometer. The micrometer is used to obtain d, the minimum displacement of which is 0.001mm. The electronic balance is with 0.01g accuracy and 1200g maximum load is used to obtain F.

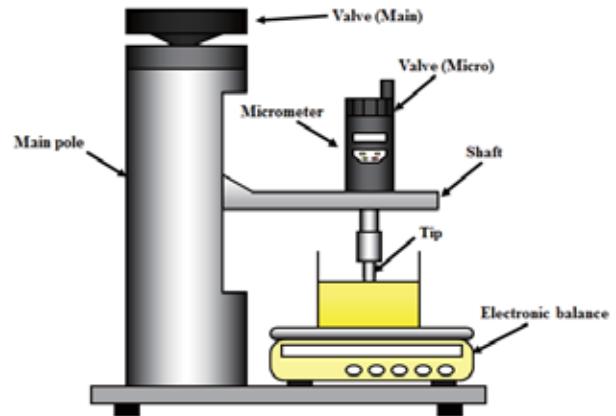# 3. Result and discussions

3.1 Intrinsic viscosity

Fig. 2 Illustration of homemade simple elastic modulus meter.

Figure 3 shows plot of the intrinsic viscosity [η] against weight fraction of Alg in whole polymers (Alg+Glt) with C_S=0.5M. The intrinsic viscosity of the mixed solution is simply the average of two components implying that each component is not influenced by the other component. That is, there is no specific interaction between the two kinds of polymers in dilute solution at 25℃. By using C and [η] for each polymers, the degree of coil overlapping of polymer chains are obtained to discuss the E values.
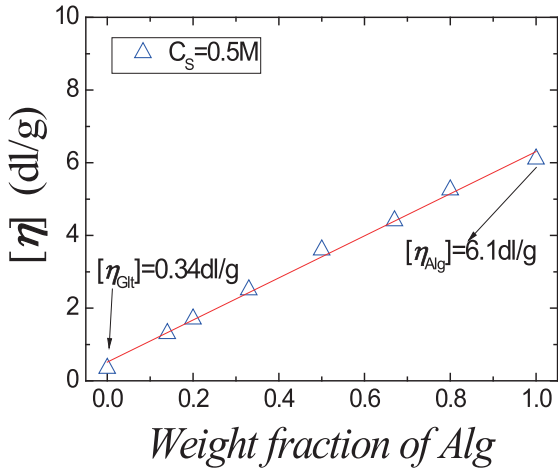
Fig. 3 Weight fraction dependence of the intrinsic viscosity for the Alg/Glt mixed solution (C_S=0.5M) at T=25℃.

Fig. 5 The phase diagram for C_{Alg}=0.5wt% and C_{Glt}=5wt% solution.

3.2 Observation of sample solution

Figure 4 shows photographs of the homogeneous solution and the phase seaparted solution at 25℃. It is clear that high C_S solution is turbid. Figure 5 shows the result of eye observation for mixed solution with different C_S. The circle denotes the homogeneous state while the cross denotes the phase separated state. At 4 ℃, all the solution became gel and macroscopically phase separated gel are observed for high C_S as shown in Figure 5. The phase boundary in Figure 5 seems to be not affected by gelation.

As briefly summarized and reported by Yonese[5], the most serious problem for preparing multicomponent hydrogels is the phase separation occurred by mixing two polymers or during gelation process. As a result, gels prepared with different concentrations and compositions showed complicated elastic behaviors, even for each piece of macroscopically phase separated gels. However, this is not the case for the system examined here as shown later. It can be concluded that the higher C_S was the main factor which caused the phase separation while phase separation is not induced by gelation.
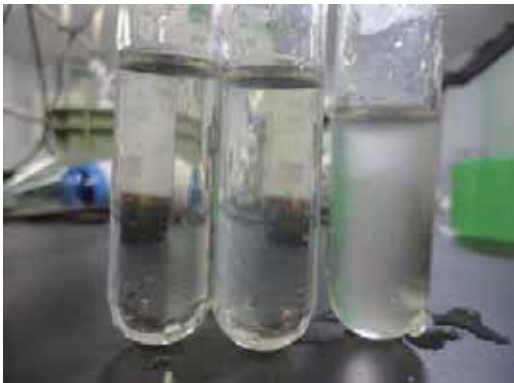
3.3 Elastic properties

Figure 6 shows an example for time t dependence behavior of F measured by electronic balance. This observation is reproducible denoting the viscoelastic nature of the samples. The relaxation behavior of F can be expressed by a single exponential decay equation.

$$F(t) = A \exp\left(-t / \tau\right) + F_\infty \qquad (3)$$

Here A is the prefactor, τ is the relaxation time, and F_∞ is the equilibrium value of the indentation force. We employ F_∞ to calculate E from equation (1).

Fig. 6 Time dependence of indentation force F. Solid line is relaxation curve of F fitted to eq (3). Broken line is the equilibrium value, F_∞, of F.

Fig. 4 Photograph of homogeneous solution and phase separated solution at 25℃. From left to right, C_S = 0.1; 0.25; 0.5M.

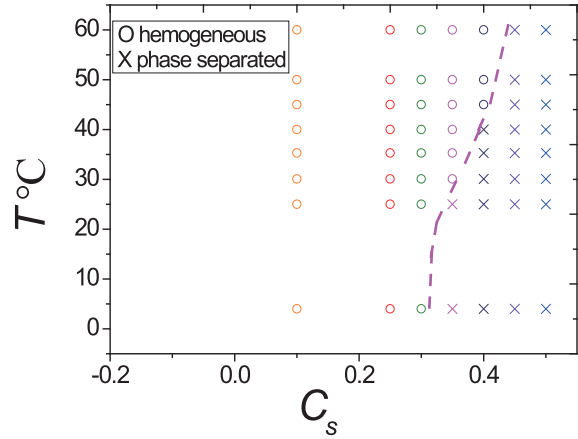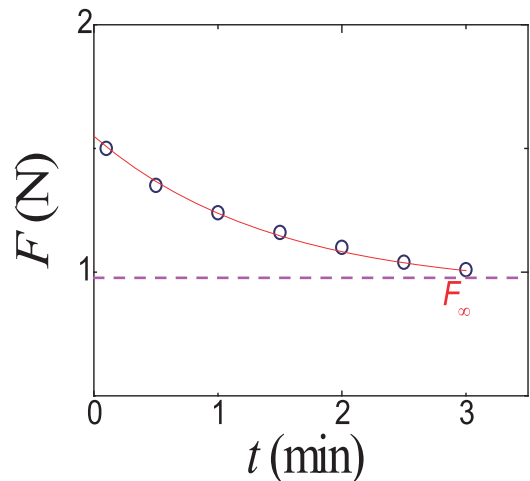Figure 7 shows plots of the elastic modulus E of Glt-Semi-IPN against degree of chain overlapping $C_{Glt}[\eta]_{Glt}$ at C_S=0.5M. (Note that only Glt undergoes gelation.) The data for single Glt gel prepared from Glt solutions (Glt simple gel) are also shown for comparison. Since the gelation is kinetically controlled by dynamics of pre-gels, the formed gels contain heterogeneity in some extent. Glt-Semi-IPN gels are slightly turbid due to the mesoscopic heterogeneity caused by phase separation. To examine non-uniformity in macroscopic scale, E are measured at several different points per a sample and the range of the data are shown by error bars in Figure 7. It is clear in this figure that the data for the Glt-Semi-IPN and Glt single gel are almost the same. It is concluded that the phase separation did not influence gelation of Glt in Glt-Semi-IPN at macroscopic level so that E values are not affected. Note that $C_{Glt}[\eta]_{Glt}\approx 3$ is the lower limit to form macroscopic gel.
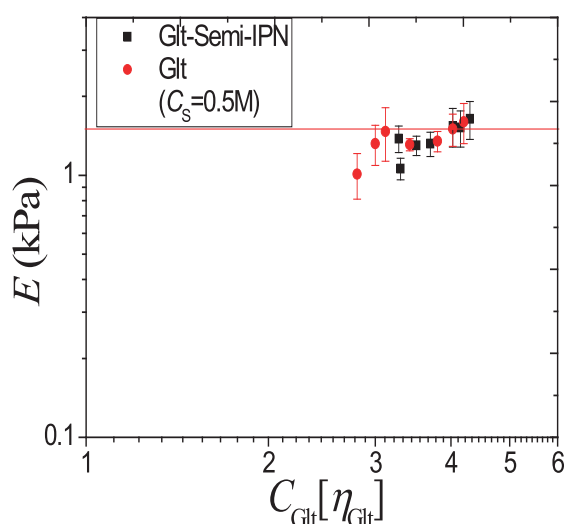

Fig. 8 Double logarithmic plots of E vs $C_{Alg}[\eta]_{Alg}$

for Alg gel prepared directly with C_S=0.5M .

Fig. 7 Double logarithmic plots of E vs $C_{Glt}[\eta]_{Glt}$

for Glt-Semi-IPN and Glt single gel with C_S=0.5M.

Figure 8 shows the elastic modulus of Alg single gels, prepared by mixing Alg solution and CaCl$_2$ solution, against degree of chain overlapping $C_{Alg}[\eta]_{Alg}$. During gelation process, syneresis occured so that C_{Alg} is determined as the final concentration calculated from final weight. As judged from its appearance, Alg single gel is much more non-uniform compared to the Glt single gel and Glt-Semi-IPN gel. Alg gel is pretty rough. As a result, E value for each sample measured at different points has much wide distribution as denoted by error bars. Macroscopic Alg gels are obtained at $C_{Alg}[\eta]_{Alg}\geq 3.6$.
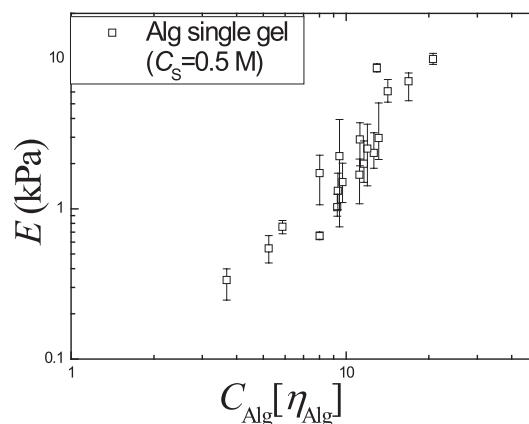
As shown in Figure 9, the IPN made from Glt-Semi-IPN with C_S=0.5M was macroscopically phase separated.

Fig. 9 Photographs of IPN made from phase separated

solution.

To check the roughness of IPN, E are plotted against initial value of degree of chain overlapping $C_{Alg}[\eta]_{Alg}$ (C_{Alg} is the initial concentration in the mixed solution of Alg) in Figure 10. Here we first measured E on both sides of the sample to analyze the differences of E. Note that when $C_{Alg}[\eta]_{Alg}\geq 6.3$, the IPN separated into two parts by itself. The upper side has larger E than the lower side denoting that Alg is highly contained in the upper side. After the measurement, IPN was separated to upper and lower pieces. Then Glt was removed from separated samples to obtain Alg gel via IPN. For upper pieces, Glt can be removed by soaking it in the NaCl solution at 40℃ and macroscopic Alg gels are obtained. For lower pieces, when Glt was removed from IPN, only a small particle like Alg gels remained. Therefore, we can conclude that upper and lower parts of IPN are Alg rich

and Glt rich phase, respectively. Coincidence of E data for lower side at $C_{Alg}[\eta]_{Alg} \geq 6.3$ in Figure 10 and E data in Figure 7 also support this conclusion.

The remained Alg gel was dried to measure the weight and the weight was subtracted from the initial weight of Alg to calculate C_{Alg} of Alg side assuming that there is no weight loss in this process.
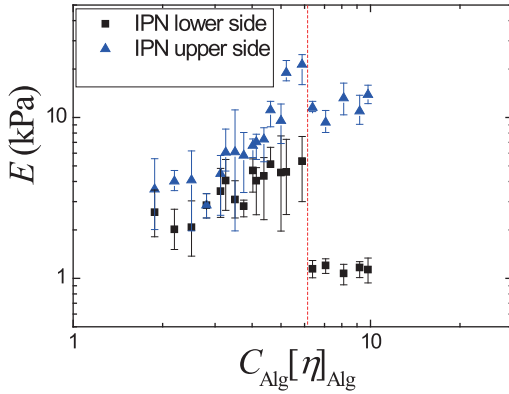

Fig. 10 Double logarithmic plots of E vs $C_{Alg}[\eta]_{Alg}$ for Alg gel prepared via IPN with C_S=0.5M. Broken line denotes the gel separation boundary of the IPN.

Finally, E data for Alg gel obtained in this work (C_S=0.5M) are compared with the data examined at data C_S=0.1M[8]. Figure 11 shows E of Alg gels plotted against degree of chain overlapping $C_{Alg}[\eta]_{Alg}$. Here the final concentration calculated by weight is used. The data for Alg single gel and via IPN falls on a straight line with slope 2, assuming simple collision of 2 chains. The roughness of Alg gels prepared via IPN and directly at higher C_S is almost the same. Alg via IPN only shows better appearance than the directly prepared ones. The Alg gels prepared with lower C_S via IPN shows narrower elastic modulus distribution than the higher ones. As a result, the lower C_S turned out to be the better condition to prepare uniform Alg gel via IPN.
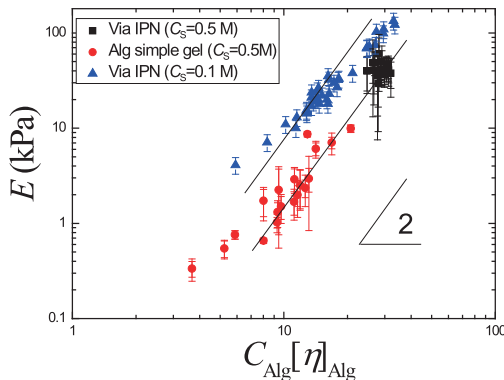
4. Conclusions

The macroscopic phase separation of Alg and Glt system is due to the high C_S. The roughness of Alg gels prepared via IPN and directly at high C_S is almost the same. The Alg gels via IPN prepared with lower C_S showed narrower elastic modulus distribution than higher ones. The lower C_S turned out to be the better condition to prepare uniform Alg gel via IPN. More systematic studies of Alg/Glt systems with different C_S will be reported elsewhere in a near future.

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Fig. 11 Double logarithmic plots of of E vs $C_{Alg}[\eta]_{Alg}$ for Alg gel prepared under different conditions.