

Viscoelastic Properties of Poly(vinyl alcohol)/Alginate Snake-Cage Hydrogels and Interpenetrating Hydrogels

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ABSTRACT: Viscoelastic properties of blend hydrogels composed of poly(vinyl alcohol) (PVA) and alginate (Alg) were studied by measuring tensile stress. Mixed aqueous solutions of PVA and Alg formed gels by repeating freeze-thaw cycles and/or by adding Ca^{2+} ions. The interpenetrating gels in which both polymers form networks showed greater elastic moduli, ultimate tensile strength and lower water contents than the snake-cage gels in which the network of one polymer (cage) traps the other polymer chains (snakes). The original samples, mixing ratio and the gelling sequence of the two polymers affected significantly the viscoelastic properties of the snake-cage and the interpenetrating gels. The equilibrium elastic moduli of the interpenetrating gels were discussed by using theoretical models of blend hydrogels. Simultaneous stress change was observed with the transition between the snake-cage and the interpenetrating gels.

KEY WORDS Poly(vinyl alcohol) / Alginate / Polymer Blends / Snake-Cage Gels / Interpenetrating Gels / Viscoelasticity / Elastic Modulus /

Hydrogels composed of biocompatible polymers are widely used in food, medical and pharmaceutical field. Viscoelastic properties of the gels are one of the most important factors for these applications. The properties can be modified versatily by blending two kinds of polymers. Using polymers which are able to form thermotropic gels, the properties of blend gels have been studied by many workers.¹⁻⁴ However, blend gels prepared from polymers which are different in the mechanism of their gelation have not been studied.

Poly(vinyl alcohol) (PVA) hydrogels prepared by freeze-thaw cycles show rubber-like elasticity.⁵ The freeze-thaw cycles induce the increase of crystalline regions which are the aggregation of ordered PVA molecules.⁶ Alginate (Alg) is a linear block copolymer of β -D-mannuronic acid and α -L-guluronic acid. Alg forms hydrogels (CaAlg) in the presence of divalent ions such as Ca^{2+} ion. The

cross-links are formed by chelate complexing between divalent ions and the carboxylate anions of guluronic acid residues.⁷

PVA and Alg show excellent compatibility in aqueous solution,⁸ and their hydrogels possess contrastive mechanical characteristics, *i.e.*, PVA gels are soft and elastic, whereas Alg gels are rigid and brittle.⁹⁻¹¹ Therefore, novel biocompatible hydrogels having desirable viscoelastic properties are expected to be obtained by mixing them appropriately. Blend gels prepared from PVA and Alg can be classified into two groups as shown in Figure 1, *i.e.*, (1) snake cage gels¹²⁻¹⁴ in which a network of one polymer (cage) traps other free polymer chains (snakes), and (2) interpenetrating gels in which both polymers form interpenetrative networks. Two kinds of snake-cage gels can be prepared, *i.e.*, (1-1) PVA network trapping Alg chains, PVA (NaAlg), and (1-2) CaAlg network trapping PVA chains,

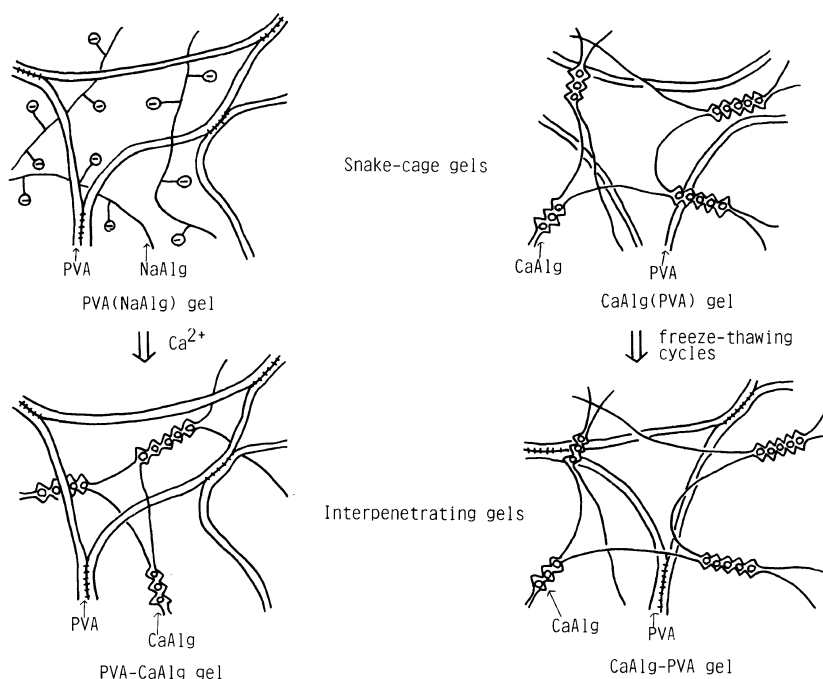


Figure 1. Schematic structures of snake-cage and interpenetrating gels.

CaAlg (PVA). The free polymer chains (snakes) are denoted in parentheses. Two kinds of interpenetrating gels can be also prepared, *i.e.*, (2-1) Alg chains in the PVA (NaAlg) gel are cross-linked furthermore by adding Ca^{2+} ion, which is denoted by PVA-CaAlg gel, and (2-2) PVA chains in the CaAlg (PVA) gel are cross-linked by repeating freeze-thaw process, which is denoted by CaAlg-PVA gel. These interpenetrating gels are different in the order of their network formation. The junctions of PVA and CaAlg gels are relatively bulky. Therefore, the subsequent network formations are considered to be affected significantly by the presence of the initial network.

EXPERIMENTAL

Materials

Two kinds of PVA samples being different degree of polymerization (DP) and saponification (DS) were used: DP[DS]=2000 [98.8%] (Katayama Chem. Ind. Co.) and DP[DS]=

2400 [99.6%] (Kuraray Co.). They were dissolved in water at 90°C , and then insoluble particles were removed by filtrating the solutions with glass filter prior to gel preparation.

Four kinds of sodium alginate (NaAlg) samples being different in DP and the fraction of guluronates (F_G) were of commercial origin (Kibun Food Chemifa Co.). Their DP[F_G] were 660 [0.84], 660 [0.50], 1170 [0.83], and 1190 [0.54]. The NaAlg samples were purified by dialyzing against distilled and deionized water for three days, followed by filtrating to get rid of insoluble substances. All other reagents were of special grade and used without further purification. Distilled and deionized water was used for the preparation of aqueous solutions.

Preparation of Blend Gels

Mixed solutions of PVA and NaAlg (total polymer concentration: 10 g/100 ml water) were prepared by dissolving arbitrary amounts

of NaAlg into PVA aqueous solutions. The solutions were poured into straight Teflon tubes (8 cm in length and 0.4 cm in internal diameter) after removing bubbles under a reduced pressure. Snake-cage gels, PVA-(NaAlg) and CaAlg(PVA), and interpenetrating gels, PVA-CaAlg and CaAlg-PVA, were prepared as follows: PVA(NaAlg); by freezing the mixed solutions filled in the tubes at -40°C for 10 h and thawing them at 7°C for 14 h, and repeating furthermore four times the freeze-thaw cycle, PVA-CaAlg; by immersing the PVA(NaAlg) gels into CaCl_2 solution (0.3 mol dm^{-3}) for seven days without taking out from the tubes, CaAlg(PVA); by immersing the mixed solutions filled in the tubes into the CaCl_2 solution for seven days, CaAlg-PVA; by repeating five times the freeze-thaw cycle of the CaAlg(PVA) gels without taking out from the tubes. Thus prepared snake-cage and interpenetrating gels were taken out from the tubes, and then CaAlg(PVA), PVA-CaAlg, and CaAlg-PVA gels were equilibrated in the CaCl_2 solution (0.3 mol dm^{-3}) and PVA-(NaAlg) gel was in water at 25°C .

Measurement

The tensile stresses of gel rods (3 cm in length and 0.3–0.4 cm in diameter) were measured under small strain ($\gamma=0.1$) according to the previous report.¹⁵ The gel rods except for PVA(NaAlg) gel were immersed in 0.3 mol dm^{-3} CaCl_2 solution and PVA(NaAlg) gel in water maintained at 25°C throughout the experiments. The diameters of the gel rods were measured by a Vernier microscope (Nakamura Works Co., Ltd.) just before measuring their stresses.

The elongation and ultimate tensile strength were measured by means of Tensilon/UTM-III-500 (Toyo Baldwin Co.) equipped with 5-kgw load cell. The extension speed was $100\% \text{ min}^{-1}$. The water contents of gels were determined from the weight change after drying at 80°C *in vacuo* for 4 h. Dried polymer densities were measured with Air Comparison Pyc-

nometer (type 930, Beckman Co.) at 25°C .

RESULTS AND DISCUSSION

Compatibility of PVA and Alg in Their Mixed Solutions and Hydrogels

The most serious problem for preparing uniform blend hydrogels is a phase separation which occurred during mixing two polymers and during gelling processes, as reported in PVA/polyethyleneglycol, PVA/poly(acrylic acid), PVA/poly(methacrylic acid), agar/BSA and agar/gelatin mixed systems.^{1,3,16–19} However, when PVA and NaAlg were mixed, no phase separation was observed for any mixing ratios because of their good compatibility.

Using the uniform mixed solutions, four kinds of blend hydrogels were prepared. Both snake-cage hydrogels, PVA(NaAlg) and CaAlg(PVA) gels, were macroscopically homogeneous. However, both interpenetrating gels, PVA-CaAlg and CaAlg-PVA gels, which were different in the order of the gelling processes, were significantly different in their appearances. The PVA-CaAlg gel was coated with a transparent gel layer, whereas CaAlg-PVA gel was not coated with such a gel layer and was macroscopically homogeneous. The outer gel layer of PVA-CaAlg gel was easily taken out of the inner opaque gel as shown in Figure 2.

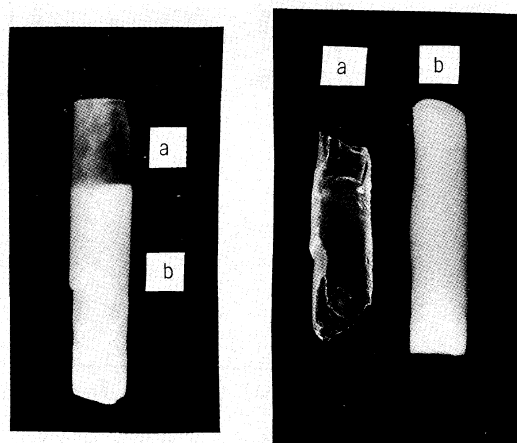


Figure 2. Multilayer structure of PVA-CaAlg gel. a, outer gel layer; b, inner gel.

The weight fractions of the outer layers to the total weights of PVA–CaAlg gels, W_{out}^T , were in the range of 1–25%, and depended on the weight fraction of Alg to total polymer of the original mixed solution, W_{alg}^S as shown in Figure 3a. W_{out}^T was found to be the greatest at about $W_{\text{alg}}^S=0.2$. Since the outer layer did not show any melt by heating at 80°C, it was speculated to be calcium alginate (CaAlg) layer. Hereafter, PVA–CaAlg gel denotes the inner gel from which the outer layer was removed.

The outer layer was considered not to be formed by phase separation but by squeeze of Alg out of the gel due to the network development of PVA and the shrinkage of the network during the freeze-thaw process.

Because of the squeeze of Alg, the weight fractions of Alg to total polymer of PVA–CaAlg gels, W_{alg} , were lower than those of the original mixed solutions, W_{alg}^S , and were obtained from the weights and the water contents of the outer gel layers and the inner

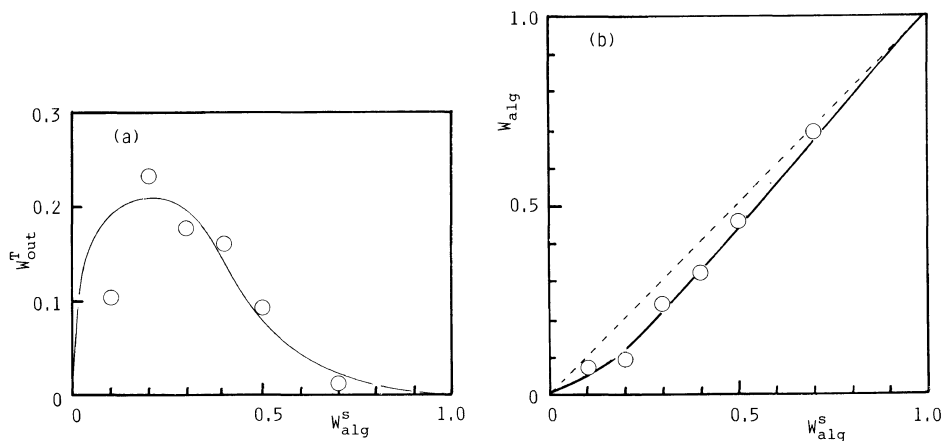


Figure 3. The effect of W_{alg} on W_{out}^T (a) and W_{alg} (b) of PVA–CaAlg gels. DP[DS] of PVA, 2000 [98.8%]; DP[F_G] of NaAlg, 660 [0.84].

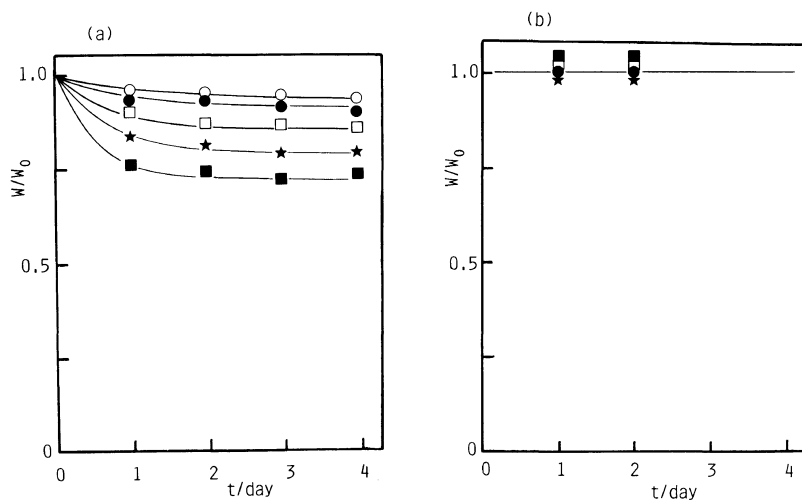


Figure 4. The weight changes of PVA(NaAlg) (a) and PVA–CaAlg (b) gels after taking out them from Teflon tubes. W , gel weight after aging; W_0 , initial gel weight. DP[DS] of PVA, 2000 [98.8%]; DP[F_G] of NaAlg, 660 [0.84]. W_{alg} : ○, 0; ●, 0.07; □, 0.09; ■, 0.24; ★, 0.32.

gels. Figure 3b shows the relationship between W_{alg} and $W_{\text{alg}}^{\text{S}}$. The values W_{alg} were found to be less by 10–50% than the values $W_{\text{alg}}^{\text{S}}$.

Figure 4 shows the weight changes of PVA(NaAlg) gels and PVA–CaAlg gels including the outer layer after they were taken out from Teflon tubes. Although no weight changes were observed for PVA–CaAlg gels, the weights of PVA(NaAlg) gels decreased by 5–25% and equilibrated in one day. The amount of the weight loss was the greatest at $W_{\text{alg}}=0.24$ in the same manner as $W_{\text{out}}^{\text{T}}$ of PVA–CaAlg gels. The weight losses are mainly ascribed to the dissolution and the release of NaAlg sol layer coating around the inner gel. Therefore, the values W_{alg} of PVA(NaAlg) gels should be equal to those of PVA–CaAlg gels obtained above. On the other hand, since CaAlg–PVA gels did not show such multilayer structure and was macroscopically homogeneous, the values W_{alg} of CaAlg–PVA and CaAlg(PVA) gels were estimated to be equal to $W_{\text{alg}}^{\text{S}}$ of them.

Viscoelastic Characteristics of Snake-Cage and Interpenetrating Gels

Figure 5 shows the typical patterns of the stress relaxations of PVA(NaAlg), PVA–CaAlg, CaAlg(PVA), CaAlg–PVA, and PVA gels. For PVA–CaAlg gels, the tensile stresses

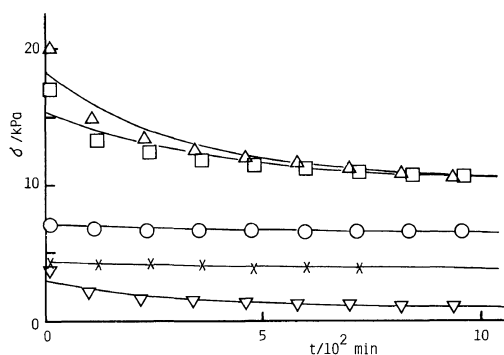


Figure 5. Stress relaxation curves of snake-cage and interpenetrating gels ($W_{\text{alg}}=0.25$) at 25°C. Δ , CaAlg–PVA; \square , PVA–CaAlg; \circ , PVA(NaAlg); ∇ , CaAlg(PVA); \times , PVA gel. DP[DS] of PVA, 2000 [98.8%]; DP[F_G] of NaAlg, 660 [0.84]. Solid curves show the values calculated using eq 1.

of the inner mixed gels were measured, because the outer CaAlg gel layers slipped down from the inner mixed gels during the measurement. PVA and PVA(NaAlg) gels showed little stress change. On the other hand, the gels in which the network of CaAlg took part in, *i.e.*, PVA–CaAlg, CaAlg(PVA), and CaAlg–PVA, showed considerable stress relaxations in the range of 10–20 h. Such long stress relaxation is an intrinsic property of CaAlg hydrogels.¹⁵ All relaxation curves were fitted by a modified Maxwell model. In this model, the tensile stress σ of a gel fixed at a constant strain γ is expressed by eq 1 as a function of time t :

$$\sigma = \{G_e + G_r \exp(-t/\tau)\} \gamma, \quad (1)$$

where G_e and $(G_e + G_r)$ are the equilibrium elastic modulus and the spontaneous elastic modulus, respectively, and τ is the relaxation time. G_e , G_r and τ for each stress relaxation curve were determined by a non-linear curve fitting method.

Figure 6 shows G_e of PVA(NaAlg), PVA–CaAlg, CaAlg(PVA), and CaAlg–PVA gels as a function of W_{alg} . The G_e values of the interpenetrating gels, PVA–CaAlg and CaAlg–PVA, were considerably greater than those of corresponding snake-cage gels, PVA(NaAlg) and CaAlg(PVA), respectively. The difference of G_e between the snake-cage and the interpenetrating gels increased with increasing W_{alg} . In the snake-cage gels, free polymer chains (snakes) affected G_e of PVA(NaAlg) and CaAlg(PVA) gels in different manners. The G_e of PVA(NaAlg) gels showed the maximum at $W_{\text{alg}}=0.1$, whereas the G_e of CaAlg(PVA) gels decreased continuously with increasing the fraction of PVA. PVA–CaAlg and CaAlg–PVA gels being interpenetrating gels showed different G_e value even if their W_{alg} were same, *i.e.*, G_e of PVA–CaAlg almost linearly increased with W_{alg} , whereas that of CaAlg–PVA shows a maximum at $W_{\text{alg}} \approx 0.7$.

The relationships between W_{alg} and the weight fractions of water (W_0^{T}) of PVA(NaAlg), PVA–CaAlg, CaAlg(PVA), and

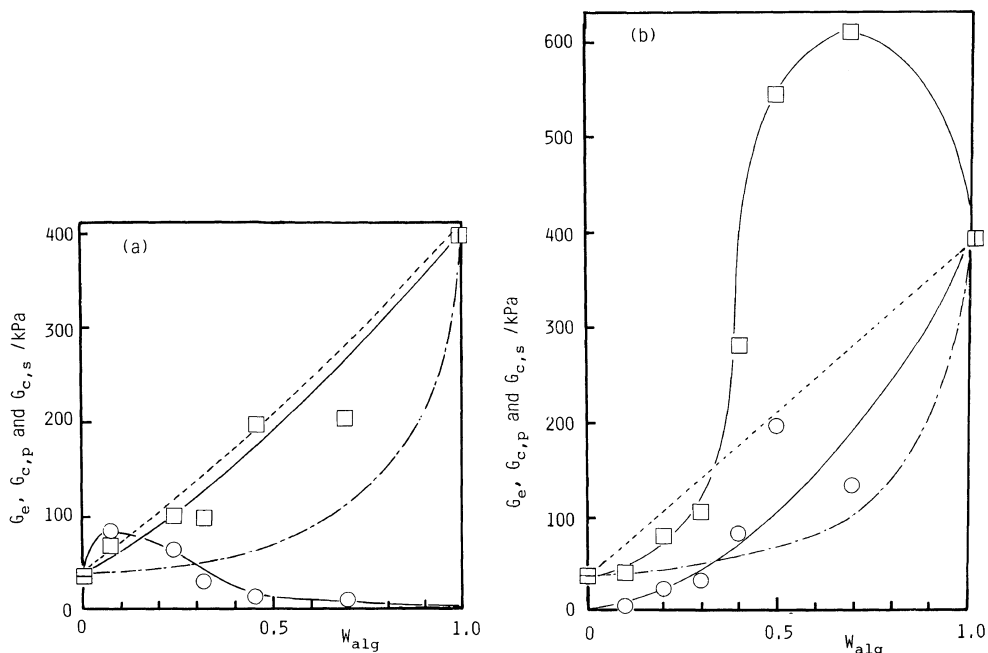


Figure 6. Equilibrium elastic modulus (G_e) vs. W_{alg} . (a) \circ , PVA(NaAlg); \square , PVA-CaAlg; \square , PVA; \square , CaAlg gel. (b) \circ , CaAlg(PVA); \square , CaAlg-PVA; \square , PVA; \square , CaAlg gel. DP[DS] of PVA, 2000 [98.8%]; DP[F_G] of NaAlg, 660 [0.84]. The curves (-----) and (-·-·-) show the values $G_{c,p}$ and $G_{c,s}$ calculated using eq 2 and 3, respectively.

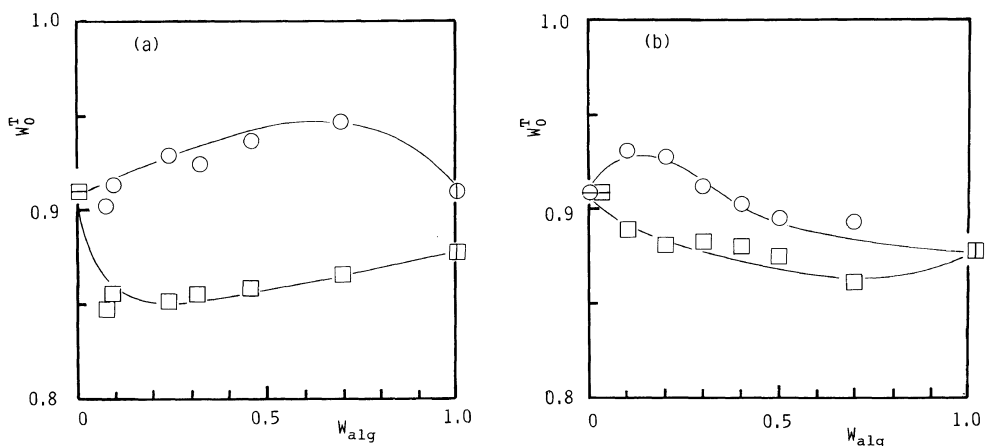


Figure 7. Water fraction (W_0) vs. W_{alg} . (a) \circ , PVA(NaAlg); \square , PVA-CaAlg; \square , PVA; \square , CaAlg gel; \odot , NaAlg solution. (b) \circ , CaAlg(PVA); \square , CaAlg-PVA; \square , PVA; \square , CaAlg gel; \ominus , PVA solution. DP[DS] of PVA, 2000 [98.8%]; DP[F_G] of NaAlg, 660 [0.84].

CaAlg-PVA gels are shown in Figure 7. The interpenetrating gels show lower water fractions by 0.03–0.07 compared to the corresponding snake-cage gels. The snake-cage gels

showed maximal W_0^T when the fraction of entrapped polymers (snakes) were in the range of 0.7–0.9, whereas the interpenetrating gels showed minimal W_0^T when the fraction of

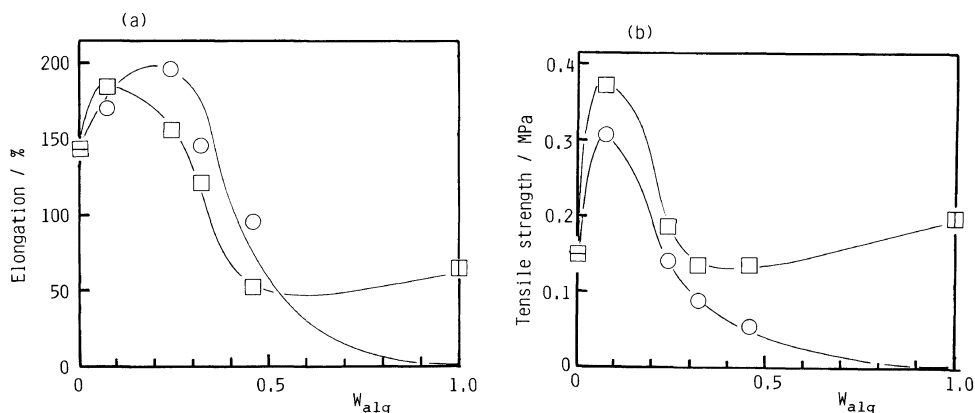


Figure 8. Elongation (a) and ultimate tensile strength (b) vs. W_{alg} . ○, PVA(NaAlg); □, PVA-CaAlg; □, PVA; □, CaAlg gel. DP[DS] of PVA, 2000 [98.8%]; DP[F_G] of NaAlg, 660 [0.84].

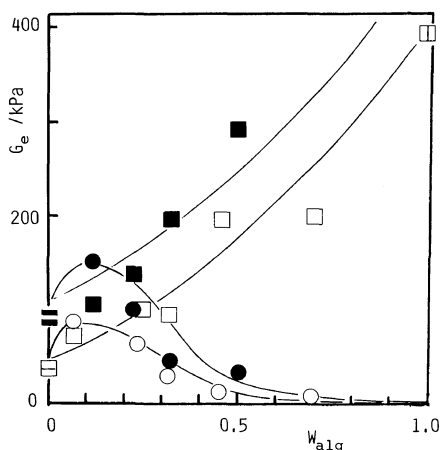


Figure 9. The effect of the original PVA sample on G_e of PVA(NaAlg) (○, ●), PVA-CaAlg (□, ■), PVA (□, ■), and CaAlg (□, ■) gels. ○, □, and □: DP[DS], 2000 [98.8%]; ●, ■, and ■: DP[DS], 2400 [99.6%].

subsequently gelled polymers were in the range of 0.1–0.3.

Figure 8 shows the elongation and the ultimate tensile strength of PVA(NaAlg) gel and PVA-CaAlg gel as a function of W_{alg} . The differences of G_e , the elongation and the ultimate tensile strength between CaAlg and PVA gels should be noticed. The value G_e of CaAlg gel was much greater than that of PVA gel. However, the elongation of CaAlg gel was much less than that of PVA gel and the ultimate tensile strength of them were almost same. It

Table I. The effect of the original NaAlg sample on G_e of PVA(NaAlg) and PVA-CaAlg gels

NaAlg		W_{alg}	G_e /kPa	
DP	F_G		PVA(NaAlg)	PVA-CaAlg
660	0.84	0.24	64.0	99.5
660	0.50	0.24	39.5	94.5
1170	0.83	0.25	36.0	139.0
1190	0.54	0.26	43.0	144.0

is remarkable that the elongation and the tensile strength of PVA(NaAlg) and PVA-CaAlg gels showed the same behavior in the range of $W_{alg} < 0.5$ and had maxima at $W_{alg} = 0.1-0.3$. The addition of small amount of Alg into PVA solution was considered to promote cross-link formation of PVA by enhancing intermolecular association between PVA chains during freeze-thaw process.

In the case of PVA-CaAlg gel, the elastic modulus increased with increasing W_{alg} as shown in Figure 6, whereas the elongation and the tensile strength decreased with W_{alg} after passing through the maxima. PVA-CaAlg gel became more rigid and brittle with increasing CaAlg fraction, whereas it became more soft and elastic with increasing PVA fraction.

Effect of Original PVA and Alg Samples

It is generally known that mechanical

strength of PVA hydrogels increases with increasing their DP and DS,^{6,20} and that of Alg hydrogels increases with increasing their DP and the guluronic acid fraction.^{21,22} Figure 9 shows the effects of DP and DS of PVA samples on G_e of PVA(NaAlg) and PVA-CaAlg gels. The values G_e of the gels prepared from the sample being of higher DP and DS showed 1.5–2.5 times greater than those from the sample being of lower DP and DS. Table I shows the effects of DP and F_G of NaAlg samples on G_e of PVA(NaAlg) and PVA-CaAlg gels ($W_{\text{alg}}=0.24\text{--}0.26$). PVA-CaAlg gels prepared from the sample being of higher DP show greater G_e values, whereas PVA(NaAlg) gel was not affected by DP. No apparent correlation between F_G and G_e was observed for PVA(NaAlg) and PVA-CaAlg gels.

Transition between Snake-Cage Gel and Interpenetrating Gel

Figure 10a shows the stress change of PVA-CaAlg gel induced by exchanging the bulk solution from 0.3 mol dm^{-3} CaCl_2 to 0.3 mol dm^{-3} tetrasodium ethylenediaminetetraacetate (EDTA-4Na) after cessation of the stress relaxation caused by the strain ($\gamma=0.1$).

The stress decreased simultaneously with the addition of EDTA-4Na and attained to equilibrium state after approximately 1 h. G_e , G_r and τ for the stress change were determined by the curve-fitting method using eq 1. The obtained G_e (40 kPa) was close to G_e of the corresponding PVA(NaAlg) gel (36 kPa). This means that the interpenetrating gel was transformed into the corresponding snake-cage gel due to the rupture of Alg junctions induced by the chelation of EDTA with Ca^{2+} . Figure 10b shows the stress change of PVA(NaAlg) gel induced by exchanging bulk solution from water to 0.3 mol dm^{-3} CaCl_2 solution. Rapid increase ($\tau=94\text{ s}$) in the tensile stress after the addition of Ca^{2+} ions was observed, but the stress change was only 0.8 kPa, and the obtained G_e was much less than G_e of the corresponding PVA-CaAlg gel. The reason why the stress increase concomitant with the transition from the snake-cage gel to the interpenetrating gel was so small might be attributed to a leakage of NaAlg during the equilibration and the stress measurement.

Effect of Gelling Process on Elastic Moduli of Interpenetrating Gels

As far as interpenetrating gels are concerned,

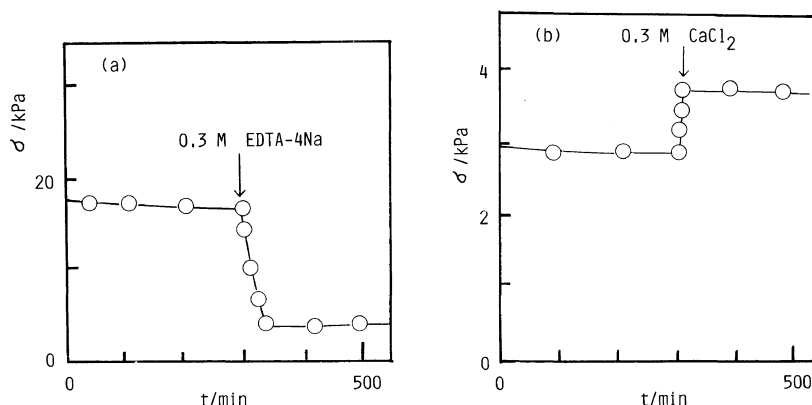


Figure 10. Stress change concomitant with transition between snake-cage and interpenetrating gels ($W_{\text{alg}}=0.25$) at 25°C . (a) Stress change of PVA-CaAlg gel by exchanging the bulk solution from 0.3 mol dm^{-3} CaCl_2 to 0.3 mol dm^{-3} EDTA-4Na. (b) Stress change of PVA(NaAlg) gel by exchanging the bulk solution from water to 0.3 mol dm^{-3} CaCl_2 . DP[DS] of PVA, 2000 [98.8%]; DP[F_G] of NaAlg, 1170 [0.83].

many theoretical models are reported which relate the elastic modulus of a blend gel to the modulus and the fraction of each component. By comparing observed elastic moduli of blend hydrogels to their theoretical elastic moduli, the homogeneity of the gels can be speculated. Takayanagi *et al.*^{2,3} proposed two simple models which are applied to heterogeneous blend polymers containing well-defined phase domains. One is the isostrain model in which each component is assumed to experience the same strain, and the other is the isostress one in which each component is assumed to experience the same stress. The models were developed to be applied to blend hydrogels by Clark *et al.*^{3,4} When the elastic moduli of the gels formed from polymer 1 and 2 are G_1 and G_2 , respectively, the elastic moduli of the blend gel for the isostrain and isostress models, $G_{c,p}$ and $G_{c,s}$, are given by eq 2 and eq 3:

$$G_{c,p} = G_1(1 - \phi_2) + G_2\phi_2 \quad (\text{isostrain model}) \quad (2)$$

$$1/G_{c,s} = (1 - \phi_2)/G_1 + \phi_2/G_2 \quad (\text{isostress model}) \quad (3)$$

where ϕ_2 is the volume fraction of the hydrogel domain formed from polymer 2. Water in the blend gel is partitioned between the network domains formed from polymer 1 and 2 according to the affinities of two polymers for water. Hereafter, PVA and Alg are denoted by 1 and 2. ϕ_2 is obtained from eq 4 according to Clark *et al.*⁴ by assuming the affinities of PVA and Alg network domains for water are equal at any mixing ratios. In deriving eq 4, the densities of both polymers, ρ_1 and ρ_2 , the blend gel, ρ_g , and water, ρ_0 , were taken into consideration, although Clark *et al.* approximated all the densities were 1.0.

$$\phi_2 = \rho_g [W_2^T/\rho_2 + \{W_2^T/(W_1^T + W_2^T)\}(W_0^T/\rho_0)] \quad (4)$$

where W_1^T , W_2^T , and W_0^T are the weight fractions of PVA, Alg, and water ($W_1^T + W_2^T + W_0^T = 1$) in the blend gel. ρ_0 is approximated

to be equal to the density of free water ($=0.997$). ρ_2 measured by the Air Comparison Pycnometer was 1.71, and ρ_g was assumed to be equal to that of CaAlg gel ($=1.03$) prepared in 0.3 ml dm^{-3} CaCl_2 ¹⁵ since the weight fractions of water W_0^T in PVA–CaAlg and CaAlg–PVA gels changed only by a few percents compared with that of CaAlg gel as shown in Figure 7.

The theoretical elastic moduli, $G_{c,p}$ and $G_{c,s}$, of PVA–CaAlg and CaAlg–PVA gels obtained from eq 2–4 are shown in Figure 6 together with their observed values G_e . It should be noted that W_{alg} of the abscissa is the weight fraction of Alg related to only polymer compositions, *i.e.*, $W_{\text{alg}} = W_2^T/(W_1^T + W_2^T)$. The theoretical values $G_{c,p}$ of the isostrain model were much greater than the values $G_{c,s}$ of the isostress model. According to the theory of Takayanagi *et al.*, elastic moduli of heterogeneous blend hydrogels are known to exist between $G_{c,p}$ (upper limit) and $G_{c,s}$ (lower limit).^{3,4} In the case of PVA–CaAlg gels, the results G_e were almost equal to the values $G_{c,p}$. This suggested that PVA–CaAlg gels are heterogeneous blend hydrogels rather than homogeneous one. On the other hand, in the case of CaAlg–PVA gels, G_e were considerably greater than $G_{c,p}$ in the range of $W_{\text{alg}} > 0.3$, and had a maximum at $W_{\text{alg}} = 0.7$. Sperling *et al.*²⁴ reported that homogeneous interpenetrating networks of elastic polymers and rigid ones showed maximal elastic moduli near the midpoint of their composition. Therefore, CaAlg–PVA gels were considered to be more homogeneous interpenetrating gels than PVA–CaAlg gels.

The reasons why the homogeneity of the blend gels is changed by altering the sequence of gelation are speculated as follows. When PVA was cross-linked first such as in PVA–(NaAlg) gels, a part of NaAlg was squeezed from the gel due to the development of PVA network formed by freeze-thaw cycles, and the microstructure of PVA(NaAlg) gel might become heterogeneous during the long freeze-

thaw process (5 days). Therefore, PVA–CaAlg gels are considered to form heterogeneous interpenetrating networks. On the other hand, when Alg is cross-linked first such as in CaAlg-(PVA) gel, the network of Alg is developed rather rapidly by the diffusion of Ca^{2+} ions, and the gels were found not to shrink and squeeze PVA chains. Therefore, free PVA chains are considered to distribute homogeneously in CaAlg network, and CaAlg–PVA gels to be rather homogeneous interpenetrating gels.

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