Structures and Physicochemical Properties of High Water Content Tough Hydrogels Prepared by Blending of Poly(vinyl alcohol) with Poly(styrenesulfonic acid) Sodium Salt

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ABSTRACT: Blend gel membranes, which have high modulus, high transparency and oxygen permeability, were prepared by blending of poly(vinyl alcohol) with poly(styrene sulfonic acid) sodium salt below 17 wt% of total polymer concentration in an autoclave at elevated temperature and pressure. Every blend gel membrane has a three dimensional honey-comb structure made by bundles or tapes whose size are about 0.1–0.2 μm . The high modulus is probably due to physically crosslinked structures formed by an interpolymer complex in addition to poly(vinyl alcohol) crystallites. The high transparency at low poly(styrene sulfonic acid) sodium salt content is caused by the small size of the bundles or tapes and high water content. Permeability coefficients of blend gel membranes are similar to that of a commercial soft contact lens.

KEY WORDS Poly(vinyl alcohol) / Poly(styrenesulfonic acid) Sodium Salt
/ Blend / Gel / Crosslink / Complex / Transparency / Oxygen Permeability /

We found that a silk fibroin membrane immersed in water/MeOH mixture was not brittle, not soluble in water at room temperature, very high transparency, and high oxygen permeability which was similar to that of a commercial soft contact lens made by poly-(hydroxyethyl methacrylate) (PHEMA). These properties are caused by the formation of many small crystallites and relatively high water content.^{1,2}

We obtained blend gel membranes which have high modulus even with relatively high water content, from a concentrated aqueous solution of poly(vinyl alcohol) (PVA) and another water-soluble polymer such as poly-(glutamic acid),^{3,4} poly(allyl amine) HCl salt,⁵ and poly(styrene sulfonic acid) sodium salt (NaPSS)⁶ prepared by an autoclave at elevated temperature and pressure. However, blend gel

membranes were turbid. Recently we obtained blend gel membranes with very high transparency and high modulus, from a clear and relatively dilute aqueous solution of PVA and NaPSS prepared using an autoclave.

We studied the fine structures, mechanical properties, thermal properties, transparency, and oxygen permeability for various NaPSS content of blend gel membranes.

EXPERIMENTAL

PVA had a molecular weight 75000, and saponification was 99.85 mol%. NaPSS of molecular weight 10000 was used in aqueous solution of 20 wt% without further purification.

PVA–NaPSS blend gel membranes were prepared by the following procedure: PVA and

NaPSS were dissolved to prepare an aqueous solution below 17 wt% of total polymer concentration (where the concentration becomes low by mixing NaPSS aqueous solution of 35 wt% in an autoclave at 2×10^5 Pa and 120°C). The highly clear solution formed was cast on a glass plate, dehydrated by electric fan at room temperature, and swollen in water. NaPSS content in the blend gel membranes prepared was of 5, 8, 12, 17, 24, and 33 wt%.

PVA gel film was cast from 15 wt% aqueous solution of PVA and then swollen in water.

Cryogenical fractured surfaces of blend gels were observed by mean of an scanning electron microscopy (Nihon-denshi JSM-25) at 20 kV and $\times 10000$.

Stress-strain curves were measured using a TENSILON UTM-II-20 at head speed of 10 mm/min.

Wide angle X-ray scattering experiments were performed using a diffractometer (RIGAKU-DENKI 2028) at a scanning rate of 1° per min. Crystallinity was evaluated from the wide angle X-ray scattering curves according to the method proposed by Hermanns.

DSC experiments were performed on a Seiko Densi instrument DSC-10 at a heating rate of 1°C min^{-1} from -50°C after cooling to observe the dissolution (melting) of the gels.

Transparency was measured using a Hitachi spectrophotometer model 100-10 at a wavelength of 500 nm.

Permeation measurement of dissolved oxygen through the membrane was done using an oxygen electrode. The permeability coefficient P [$\text{cm}^3(\text{STP})\text{cm cm}^{-2}\cdot\text{s}^{-1}\cdot\text{cmHg}^{-1}$] was calculated from steady-state current of the permeation curve.

RESULTS AND DISCUSSION

Figure 1 shows scanning electron micrographs of the freeze-dried blend gel membranes. Every blend gel membrane has a three dimensional honey-comb structure made by bundles or tapes whose size are about 0.1–0.2

μm . The water content of these blend gel membranes increases with blending NaPSS (Figure 2). In other words, polymer concentration of the blend gel membrane decreases with blending NaPSS. As a result, the three dimensional honey-comb structure becomes rough with blending NaPSS as seen in Figure 1.

The blend gel membranes were highly elastic having a fracture strain above 400%, while the fracture strain of PVA gel film was 200%. This high fracture strain of blend gel membrane probably resulted from the high water content.

Figure 3 shows Young's modulus as a function of NaPSS content. The decrease of Young's modulus with increasing NaPSS content is caused by the formation of the rough honey-comb structure as seen in Figure 1. Young's moduli of these blend gel membranes are higher than that of PVA gel prepared by repeated freezing and thawing.⁷ This high modulus is due to many physically crosslinked points even with relatively high water content. There were only PVA crystal diffraction peaks in the X-ray diffraction curves of the freeze-dried blend gel membranes. Each crystallinity of the freeze-dried blend gel membrane was about 40% (Figure 4). The PVA crystallites form crosslinks in the blend gel membranes. Previously we clarified that the PVA blend gel membranes had another type of physical crosslinks due to the interpolymer complex.^{3–6} Thus we studied whether the interpolymer complex of PVA with NaPSS exists in blend gels. Figure 5 shows the dependence of the DSC thermogram of dissolution for the blend gel membranes on NaPSS content. Two broad endothermic peaks appear to overlap. One broad peak is observed around 60°C , and the other one overlaps around 90°C . The lower broad peak is caused by dissolution of PVA crystallites which act as physical crosslinks in blend gel membranes. This is because PVA crystallites dissolve in a similar temperature region in the case of the PVA gel.⁷ This suggests that PVA crystallites grow at a very high rate in blend hydrogels.

Figure 1. Scanning electron micrographs.

Figure 2. Dependence of water content on NaPSS content.

Figure 3. Dependence of Young's modulus on NaPS content.

There were no peaks in the DSC curve of the concentrated aqueous solution of NaPSS, which does not form gels. Another broad peak

was found around 90 °C in the DSC curve of each blend gel membrane as described above. Thus, the broad peak overlapped around 90 °C

Figure 4. Dependence of crystallinity on NaPSS content.

Figure 6. Dependence of absorbance on NaPSS content.

Figure 5. DSC thermogram of blend gel membranes. NaPSS content (wt%); —, 5; ·····, 8; ———, 12; ———, 17; ———, 24; ———, 33.

is due to another physically crosslinked structure in the blend gel membranes, probably formed by intermolecular hydrogen bonds between hydroxy groups of PVA and strongly interacting SO_3Na groups of NaPSS. The hydrogen bonds act like a zipper, and consequently form an interpolymer complex^{8,9} even in this concentration of solution. These results mean that PVA and NaPSS are miscible with each other in the amorphous region of the transparent blend gel. This is similar to the cases of the coagulated gel prepared by blending of PVA with poly(glutamic acid),^{3,4} poly(allyl amine) HCl salt,⁵ and NaPSS.⁶ With blending NaPSS, such crosslinks formed by the interpolymer complex should increase, and Young's modulus increase. However, as seen in Figure 3 Young's modulus decreases with increasing NaPSS content. This means that Young's modulus mainly depends on the water

content or roughness of the three dimensional honey-comb structure in the blend gels, and not the number of interpolymer complex crosslinks. It is noteworthy that the area of the broad dissolution peak by the interpolymer complex is almost the same in every blend gel. This means that there is an upper limit to form the interpolymer complex in the NaPSS content, and an excessively blended NaPSS exists in weakly interacted state.

To study transparency, absorbance (α), *i.e.*, attenuation of light through the gel membrane, calculated from the logarithm of {intensity of light source (T_0)/intensity of transmitted light (T)} at the wavelength of 500 nm, was plotted as a function of NaPSS content (Figure 6). α is very small below a NaPSS content of 12 wt%. Because the size of bundles (about 0.1–0.2 μm) of every blend gel (see Figure 1) is very small and the blend gels have high water content as seen in Figure 2, α increases drastically above 17 wt%. According to Lambert and Beer, α is given by eq 1.

$$\alpha = \mu Cl \quad (1)$$

where μ , C , and l are the molecular absorption coefficient, concentration of solute and thickness of membrane, respectively. In this case, C is total polymer concentration, which decreases with blending NaPSS, and l is constant. Thus if μ is constant, α should decrease with increasing NaPSS content. However α increases with NaPSS content as seen in Figure 6. This indicates that the absorption of visible light is mainly caused by increase of the mean value

Figure 7. Dependence of permeability coefficient on water content. Δ , PHEMA copolymer; $\circ$, silk fibroin; $\star$, PVA-NaPSS blend gel membranes; $\star$, PVA.

of μ with the blending polar SO_3Na group of NaPSS.

According to Kaji *et al.*,¹⁰ the best condition to obtain high transparent PVA gel, prepared by dissolving PVA in a dimethyl sulfoxide-water mixture above a critical gelation concentration, is quenching below -20°C , while in this study the polymer concentration of initial mixture of blend was most important to form a high transparent hydrogel rather than quenching.

The permeation of oxygen of the gel membrane was measured using an oxygen electrode.¹¹ The permeability coefficients (P) are plotted as a function of water content with the data of silk fibroin and PHEMA membranes¹ (Figure 7). P of every blend gel membranes is larger than those of silk fibroin membranes and PVA gel film, and similar to the highest value of PHEMA copolymer. Usually, the more water, the higher P becomes, and P of oxygen depends on the amount of free water. Although the blend gel membranes had higher water

content than PHEMA, the P is not close to that of water. This suggests that water in these gels is bound or bonded by polar and highly hydrophilic SO_3Na groups of NaPSS polymer in the blend gel membranes. It is noteworthy that P decreases with increasing water content for blend gel membranes. This also results from increasing bound and bonded water with blending NaPSS.

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